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The evolution from disordered Ad to ordered $2M_1$ white K-mica polytype in low-temperature metamorphosed sedimentary rocks

by *Michael Dalla Torre*[1,2] and *Martin Frey*[1]

Abstract

Six sets of samples from five low-temperature regional metamorphic regions were investigated in order to determine the evolution of white K-mica polytypes as a function of temperature. The data show that disordered group A structures (Ad) associated with small amounts of mixtures of 1M and $2M_1$ structures occur in the diagenetic zone. The true 1Md structure was found to be less common than suggested by previous authors. At anchizonal grades, Ad and 1Md structures disappear and mixtures with variable amounts of 1M and $2M_1$ polytype prevail. In 90% of the samples the concentration of $2M_1$ varies between 70 and 90% at this grade. The largest proportions of the 1M structure are 40% and were found in a sample belonging to the diagenesis/anchizone boundary. At the onset of the epizone, 100% $2M_1$ are reached in most cases including a few exceptions. Our data suggest that the polytype transformation from Ad structures at the diagenetic zone to a mixture of 1M and $2M_1$ at the anchizone to 100% $2M_1$ at the epizone is a function of temperature and can be used as an indicator of grade in sedimentary rocks metamorphosed at low-temperature conditions.

Keywords: white K-mica, illite, polytype, X-ray diffraction, Central Alps, SW-England, Jämtland, New Zealand.

Introduction

In order to determine different structures of white K-mica, several methods have been presented in the literature. In earlier studies, the 1Md structure was identified by the absence or low intensity of diagnostic 1M reflections (YODER and EUGSTER, 1955; LEVINSON, 1955) or by using different peak intensity ratios (VELDE and HOWER, 1963; REYNOLDS, 1963; MAXWELL and HOWER, 1967). Based on the methods developed in these early studies, several workers concluded that 1Md is the dominant structure in diagenetic samples (for a review, see FREY, 1987). Other criteria to identify disordered white K-mica material were presented by BAILEY (1988) and were later shown to be useful by AUSTIN et al. (1989): (1) the elevated background in X-ray powder diffraction (XRPD) patterns between 20 and 33° 2Θ CuKα has been attributed to the presence of 1Md polytype (DRITS et al., 1984; EBERL et al., 1987; BAILEY, 1988; AUSTIN et al., 1989), and (2) the 1Md polytype lacks discrete *hkl* reflections with $k \neq 3n$ (BAILEY, 1988). However, in samples where an elevated background is found in XRPD patterns and the nature of the ordered polytype cannot be established or a mixture of polytypes occurs, 1Md is no longer a useful term. This is because disorder is possible in all polytypes (AUSTIN et al., 1989) and, therefore, BAILEY (1988) proposed that the term Ad (disordered group A micas) is used in such cases. Although to date there is no method to quantitatively measure the content of Ad structures in a sample that contains mixtures of polytypes, estimates of the relative importance of disordered versus 1M and/or $2M_1$ structures can be made using the above-mentioned criterion.

In order to determine relative proportions of the ordered 1M and $2M_1$ polytype, recent studies (CAILLÈRE et al., 1982; MASSONNE and SCHREYER,

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1986; TETTENHORST and CORBATO, 1993) used intensity ratios of different diagnostic 1M and $2M_1$ reflections. Because quantitative determination of white K-mica polytypes is difficult, due to sample preparation procedures and their effects on XRPD patterns as well as due to sophisticated evaluation of specific diagnostic reflections, DALLA TORRE et al. (1994) experimentally reinvestigated the different methods developed by various researchers. The authors found that using the sample preparation procedure after HANDSCHIN and STERN (1989), the method by CAILLÈRE et al. (1982) yielded the best results to determine relative amounts of $2M_1$ and 1M in absence of disordered polytype structures. However, their method is not applicable when disordered structures are present in a sample.

In this study, we used the criterion by BAILEY (1980, 1988) and AUSTIN et al. (1989) to determine the presence of disordered structures in a set of samples from different low-temperature metamorphic regions. In order to distinguish between the 1M and $2M_1$ white K-mica polytype, as well as to determine their relative amounts in samples free of disorder, the procedures proposed by DALLA TORRE et al. (1994) were applied. To date, there is no systematic study that investigated the distribution of different polytype structures in regionally metamorphosed rocks using the recently developed methods. Therefore, the goal of this investigation is to present data on the evolution of disordered to $2M_1$ white K-mica structures in sedimentary rocks metamorphosed under low-temperature conditions.

Experimental procedures

Fractions of the < 2 μm fraction of 70 samples were investigated using XRPD on a Siemens D5000 diffractometer. Most of the samples studied were kindly provided by H.J. Kisch (< 2 μm fraction) and L.N. Warr (rock chips), and were previously described by these authors (KISCH, 1980 a; 1980 b; 1994; WARR and RICE, 1994; WARR, 1996). Samples denoted with MF, F or L were collected by M. Frey and were described in HUNZIKER et al. (1986). ILC samples were collected by S. Krumm.

About 70 to 200 grams of MF, F, and L samples as well as those provided by L.N. Warr were ground in a tungsten-carbide swing-mill for 20 seconds. Samples containing calcite were treated with acetic acid. Fractions of the < 2 μm fraction were obtained using settling tubes and millipore filters and were Ca-saturated. Mounts for the measurement of illite crystallinity (IC) values were prepared as sedimentation slides using 5 mg of material per cm^2 of sample surface. IC values were determined on air-dried specimens only. IC values for the diagenesis/anchizone and the anchizone/epizone boundary are 0.42° and 0.25° $\Delta 2\Theta$ CuKα, respectively (see FREY, 1988).

Disoriented mounts for the determination of polytypes were prepared using the procedure by HANDSCHIN and STERN (1989). Because this original publication may not generally be available, the reader is referred to DALLA TORRE et al. (1994). Unoriented mounts of diagenetic samples and of samples with an elevated background in XRPD patterns between 20 and 33° 2Θ CuKα of air-dried mounts were glycolated for 128 hours. This procedure was proposed by AUSTIN et al. (1989), who found that diagnostic reflections of ordered polytypes are better resolved in XRPD patterns of ethylene-glycolated than of air-dried mounts.

According to the recommendations outlined by DALLA TORRE et al. (1994), a calibration curve was experimentally determined in order to quantitatively measure the relative proportions of 1M and $2M_1$. Different proportions of 1M and $2M_1$ white K-mica polytype were mixed together according to the procedures given by these authors. A description of the 1M and $2M_1$ polytype used may be found in DALLA TORRE et al. (1994) and SCHWANDER et al. (1968), respectively.

The XRPD measurements were performed on a Siemens D5000 diffractometer equipped with a graphite monochromator and a SICOMP 32–50 computer using the Siemens SOCABIM Diffrac AT V3.2 software. The divergence slits were variable during the measurements, whereas the secondary slit was fixed (0.2 mm). Earlier IC data were obtained on a Philips diffractometer at Basel University using CuKα radiation, a Ni primary filter, and divergence slits fixed at 2°. The receiving slit was fixed at 0.1 mm. The measurement conditions are given in table 1. According to the recommendations by DALLA TORRE et al. (1994), the 1M [112] and the $2M_1$ [025] reflections and the ratio $2M_1/(2M_1 + 1M)$ were used to determine the relative proportions of the two polytypes in samples free of disordered white K-mica structures. The areas of diagnostic peaks were estimated using computer-aided evaluation. In most cases, a single peak computation was applied. In a few samples, however, superposition of a small K-feldspar reflection on the 1M [112] reflection was observed. In these cases, the white K-mica reflections were resolved by mathematical deconvolution techniques using a Pearson VII function.

Tab. 1 Conditions for x-ray powder diffraction (XRPD).

diffractometer	measurement	2Θ range		scan speed	increment
		min	max	°2Θ min^{-1}	°2Θ
D5000	IC	2.0	20.0	0.10	0.05
D5000	< 2 μm mineral assemblage	20.0	42.0	1.20	0.02
D5000	< 2 μm mineral assemblage	42.0	48.0	0.75	0.02
Philips	IC	2.0	20.0	2.00	
D5000	$2M_1$ calibration	28.3	31.3	0.10	0.02
D5000	$2M_1$	18.0	33.0	0.10	0.02
D5000	$2M_1$ diagenetic samples	8.0	55.0	0.10	0.02

Geological settings of the different regions

70 samples from five different metamorphic settings were investigated in this study. The mineral assemblages of < 2 μm fractions are shown in table 2. K-feldspar, albite, and dolomite are present as minor or trace amounts in the < 2 μm fractions only and did therefore not hinder XRPD evaluation of diagnostic 1M and $2M_1$ reflections. Sample localities can be found in table 2. In the following, we outline briefly the geological settings of the different sets of samples. For additional information, the reader is referred to the publications listed in table 2.

Two sets of the samples are from Switzerland and were previously studied by KISCH (1980b) and HUNZIKER et al. (1986). The first set of samples was provided by H.J. Kisch and contains shales associated with Taveyanne graywacke or flysch. The shales and associated rock types are of Upper Eocene and Lower Oligocene age and represent the youngest clastic sedimentary rocks in the North Helvetic nappes of Switzerland. KISCH (1980b) provides data on diagnostic metamorphic minerals in the different rock types as well as vitrinite reflectance values for some samples. IC values obtained during the course of this study cover the range from the diagenetic zone to the epizone (Tab. 2).

The second set of samples, previously described by HUNZIKER et al. (1986), is from a Mesozoic sequence of sedimentary rocks that can be traced from the Jura Mountains beneath the Swiss Molasse Basin to the Glarus Alps. The sequence is largely undeformed in the Jura Mountains and probably was never buried more than 500 m. In the Molasse Basin, the sequence is covered by up to 5000 m rock that reached minimum temperatures of 100 to 150 °C (HUNZIKER et al., 1986). In the Glarus Alps, the Mesozoic sequence is largely deformed and experienced anchizonal to epizonal metamorphic conditions. The majority of the samples are from a Triassic red-bed formation referred to as Keuper in the Jura Mountains and Quartenschiefer in the Alps. IC values (Tab. 2) cover the whole range from the diagenetic zone to the epizone and are associated with increasing metamorphic conditions from the north to the south of the sequence (HUNZIKER et al., 1986).

Another set of samples also provided by H.J. Kisch is from Jämtland, Sweden, and was previously described by this author (KISCH, 1980a, 1994). The samples studied belong to the Jämtland Supergroup, which is a late-Precambrian and Lower-Paleozoic sedimentary sequence that covers a Precambrian basement. Three main tectonic divisions may be distinguished within the Jämtland Supergroup: these are (i) the autochthon of undeformed Precambrian basement and Cambro-Ordovician platform sediments, (ii) the parautochthonous cover nappes that include the entire Precambrian and Lower-Paleozoic sequence (Jämtland nappes), and (iii) the allochthon of the major long-transported nappe units including basement and cover. The samples investigated in this study are from the parautochthonous Lower Paleozoic units within the Jämtland nappes and have Middle Cambrian to Upper Ordovician, and Silurian ages (KISCH, 1980a). The Silurian sediments represent a largely undeformed sequence and cover weakly foliated Upper Ordovician to Middle Cambrian units. In addition, there is an increase in metamorphic grade from the diagenetic autochthon westward toward the allochthonous sequences.

Most samples from the South Island of New Zealand were provided by L.N. Warr. The South Island consists of accreted terranes that were metamorphosed during Jurassic and Cretaceous times (COOMBS et al., 1976). One of the most extensively investigated areas is the Torlesse terrane, which consists mostly of Permian to early Cretaceous graywackes intercalated with shales. The shales studied are from four different metamorphic grades: zeolite, prehnite-pumpellyite, pumpellyite-actinolite, and greenschist facies. IC values decrease with increasing metamorphic

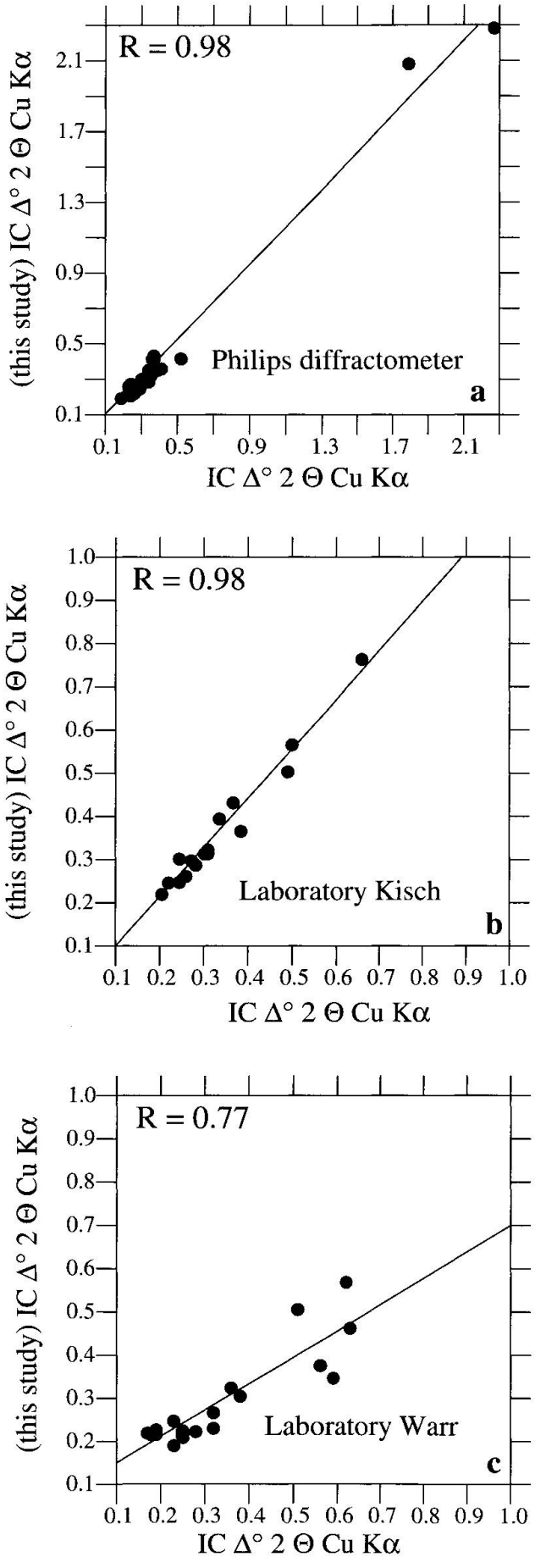
Tab. 2 Localities, mineral assemblages of fractions < 2 μm, IC, and $\frac{2M_1}{2M_1+1M}$ of samples investigated in this study.

sample #	locality	ms	chl	qtz	dol	hem	ab	kfs	i/s	stp	sm	other	IC‡	IC this study	$\frac{2M_1}{2M_1+1M}$	reference
Jämtland																
N78-59B	N Norderän	○	○	○			○						.31	.31	.58	KISCH (1980a; 1994)
N78-66B	Brännåsen, NE Östersund	○	○	○			○						.39	.37	.68	KISCH (1980a; 1994)
N78-47A	Mörsil-Järpen	○	○	○			○						.25	.30	.71	KISCH (1980a; 1994)
N78-47B	Mörsil-Järpen	○	○	○			○						.27	.30	.75	KISCH (1980a; 1994)
N92-7	Röde, N Alsensjön	○	○	○			○						.26	.26	.89	KISCH (1980a; 1994)
N92-9	Undersåker	○	○	○			○						.21	.22	.97	KISCH (1980a; 1994)
N92-10	Undersåker	○	○	○			○	○					.22	.25	.97	KISCH (1980a; 1994)
N92-13C	Änge	○	○	○			○						.31	.32	.73	KISCH (1980a; 1994)
Dachschiefer																
Z74-3B	Kiental	○	○	○			○		○				.50	.57	Ad	KISCH (1980b)
Z75-22C	Mus, Urnerboden	○	○	○			○						.25	.25	.84	KISCH (1980b)
Z75-29B	Oberalp-Äsch, Schächental	○	○	○			○						.30	.31	.95	KISCH (1980b)
Z75-34B	Oberalp-Äsch, Schächental	○	○	○			○						.28	.29	.85	KISCH (1980b)
Z75-40C	Grube Gasperini, Seedorf	○	○	○			○						.34	.39	.75	KISCH (1980b)
Z75-40D	Grube Gasperini, Seedorf	○	○	○			○						.37	.43	.75	KISCH (1980b)
Z75-85H	Sattelhorn, Kandergrund	○	○	○			○		○				.66	.76	Ad	KISCH (1980b)
JZ75-90A	Balme, W Kandergrund	○	○	○			○						.49	.50	.82	KISCH (1980b)
Keuper Quartenschiefer																
F103	Frick	○		○	○		○	○	○					1.23	Ad	this study
F108	Frick	○	○	○	○		○	○	○					1.96	Ad	HUNZIKER et al. (1986)
F176	Frick	○		○	○		○	○	○				2.27	2.28	1Md	HUNZIKER et al. (1986)
L10	Lindau	○	○	○	○		○	○	○					1.74	1Md	this study
L12	Lindau	○	○	○	○		○	○	○				1.79	2.08	Ad	HUNZIKER et al. (1986)
L17	Lindau	○		○	○		○	○	○					1.30	Ad	HUNZIKER et al. (1986)
MF131	Garvera	○	○	○	○		○					ctd		.42	1.00	this study
MF4	Quarten	○	○	○	○	○							.52	.42	Ad	HUNZIKER et al. (1986)
MF15	Quarten	○	○	○	○			○	○					.57	Ad	this study
MF20	Flissen	○	○	○	○	○			○					1.15	Ad	HUNZIKER et al. (1986)
MF23	Flissen	○		○	○	○							.37	.43	.42	HUNZIKER et al. (1986)
MF34	Schwarzstöckli	○	○	○	○	○							.37	.41	.89	HUNZIKER et al. (1986)
MF341	Panüöl	○		○	○	○							.33	.28	.77	HUNZIKER et al. (1986)
MF48	Limmernboden	○	○	○	○	○							.23	.26	1.00	HUNZIKER et al. (1986)
MF52	Bifertengletscher	○	○	○	○	○								.22	.61	this study
MF53	Bifertengletscher	○	○	○	○	○							.29	.25	1.00	HUNZIKER et al. (1986)
MF54	Bifertengletscher	○	○	○	○	○							.27	.23	1.00	HUNZIKER et al. (1986)
MF56	Schafleger	○	○	○										.51	.58	this study
MF58	Schafleger	○	○	○	○	○								.42	.91	this study
MF59	Schafleger	○	○	○	○	○							.41	.36	.90	HUNZIKER et al. (1986)
MF60	Rot Rus	○	○	○	○	○							.30	.27	.85	HUNZIKER et al. (1986)

Tab. 2 continued.

sample #	locality	ms	chl	qtz	dol	hem	ab	kfs	i/s	stp	sm	other	IC‡	IC this study	$\frac{2M_1}{2M_1+1M}$	reference
MF65	Rusenbach	○	○	○	○	○							.35	.32	.86	HUNZIKER et al. (1986)
MF703	Chrumm Bach	○	○	○	○	○							.39	.35	1.00	HUNZIKER et al. (1986)
MF71	Frittern	○	○	○	○	○	○						.30	.30	1.00	HUNZIKER et al. (1986)
MF73	Bützistock	○	○	○	○	○	○	○						.38	.91	this study
MF731	Panixer Rotstock	○	○	○		○							.19	.19	1.00	HUNZIKER et al. (1986)
MF74	Bützistock	○	○	○	○	○							.34	.29	.97	HUNZIKER et al. (1986)
MF75	Bützistock	○	○	○		○								.32	.83	this study
MF82	Curaglia	○		○	○	○	○							.21	1.00	HUNZIKER et al. (1986)
New Zealand																
NZ4	1.1* Deep Creek (Waimate Gorge)	○	○	○					○				.28	.22	.70	WARR (1996)
MF2839	1.1* Deep Creek (Waimate Gorge)	○	○	○			○	○					.26	.22	.66	this study
MF2843	1.3B* Benmore dam	○	○	○			○	○	○				.36	.41	Ad	this study
NZ8	1.3C* Benmore dam (shore platform)	○	○	○			○	○	○				.51	.51	.69	WARR (1996)
MF2846	1.3C* Benmore dam (shore platform)	○	○	○			○	○					.34	.35	.70	this study
NZ9	1.4* Dalrachine Bridge (Longslip Creek)	○	○	○			○	○			○		.32	.27	.55	WARR (1996)
MF2848	1.4* Dalrachine Bridge (Longslip Creek)	○	○	○			○	○					.24	.27	.64	this study
MF2850	1.5* Longslip Creek	○	○	○			○	○					.24	.21	.98	this study
NZ15-P	1.7* Lindis River (S Goodger Road)	○	○	○			○	○					.19	.23	.94	WARR (1996)
NZ17	2.1* Shotover River Bridge	○	○	○			○	○					.23	.25	1.00	WARR (1996)
MF2856	3.1* Lake Howden	○	○	○			○	○					.23	.22	.89	this study
NZ29	4.0* Rocky Point Quarry, Mossburn	○	○	○			○	○	○		○	lmt	.62	.57	Ad	WARR (1996)
NZ42	5.5* Taieri Mouth	○	○	○			○	○		○	○	pmp	.23	.19	1.00	WARR (1996)
NZ43	Lake Hawea to Lake Wanaka road section	○	○	○			○	○					.25	.21	1.00	WARR (1996)
NZ45	Lake Hawea to Lake Wanaka road section	○	○	○			○	○			○		.18	.21	1.00	WARR (1996)
NZ46	Lake Hawea to Lake Wanaka road section	○	○	○			○	○		○			.19	.22	1.00	WARR (1996)
SW England																
SW1	Widemouth Bay	○	○	○			○		○				.63	.46	.61	WARR and RICE (1994)
SW4	Portgaverne	○	○	○				○				pg	.38	.30	.93	WARR and RICE (1994)
SW6	Trebarwith Strand	○	○	○			○						.25	.22	1.00	WARR and RICE (1994)
Rheinisches Schiefergebirge																
ILC1	Adorf	○	○	○			○						.36	.32	.87	KRUMM (written comm., 1995)
ILC3	Well Eibach	○	○	○			○						.56	.38	.56	KRUMM (written comm., 1995)
ILC4	N Koblenz	○	○	○			○						.32	.23	.74	KRUMM (written comm., 1995)
ILC6	railway station Oos	○	○	○			○						.59	.35	.47	KRUMM (written comm., 1995)

Explanations: * denotes number of excursion stop in COOMBS and COX (1991), ‡ denotes IC data from previous studies (see text), ms = white K-mica, chl = chlorite, qtz = quartz, dol = dolomite, hem = hematite, ab = albite, Kfs = K-feldspar, i/s = mixed-layer illite/smectite, sm = discrete smectite, lmt = laumontite, stp = stilpnomelane, pg = paragonite, pmp = pumpellyite, ctd = chloritoid.



grade from the zeolite to the greenschist facies (see Tab. 2, and WARR et al., 1996).

The SW samples are from a NE–SW trending traverse of the Variscan low-grade metamorphic belt of north Cornwall, south-west England (WARR and RICE, 1994). The diagenetic sample SW1 was taken from an Upper Carboniferous sequence, whereas samples SW4 and SW6 are Devonian in age. The SW samples were proposed to be used as interlaboratory standards for IC measurements (see WARR and RICE, 1994).

The samples ILC1, ILC3, and ILC5 are from the Rheinisches Schiefergebirge in Germany. Specimen ILC1 was collected near Adorf, sample ILC2 is from east and sample ILC5 from south-west of Dillenburg, Germany. Samples ILC1 and ILC3 are Upper Devonian in age, wheras sample ILC5 is of Lower Carboniferous age. The specimen ILC4 was collected north of Koblenz, Germany (all information by S. Krumm, written comm. 1995).

Results and discussion

IC DATA

In the first part of this section, we will briefly discuss IC data obtained by previous researchers and this study. The correlations between IC values obtained at Basel University and those found in other laboratoires are shown in figure 1. The best correlation coefficients were obtained with the data provided by Kisch (written comm., 1995) and with earlier data obtained at Basel University using the Philips diffractometer. A smaller correlation coefficient is observed between our data and those published by WARR and RICE (1994) and WARR (1996). Their IC values are generally larger than those obtained in this study. These observations suggest that the IC values for the diagenesis/anchizone and anchizone/epizone boundaries for data from Kisch (written comm., 1995) are very close to those from our laboratory using both the Siemens D5000 and the Philips diffractometer. Although WARR and RICE (1994) adopted limits of the anchizone of 0.42° and 0.25° Δ2Θ CuKα, our data are consistent with 0.37° and 0.23° Δ2Θ CuKα, respectively. In addition, compared to the plots in figure 1A and B, figure 1C shows a rela-

Fig. 1 Correlations between illite crystallinity (IC) data obtained in different laboratories and this study. (a) Philips diffractometer (Basel University), (b) Kisch (written comm., 1995), (c) WARR and RICE (1994) and WARR (1996).

tively large scatter. The scatter and variability in correlations and thus in turn the different limits for the anchizone obtained from figure 1B and C presumably arose from different rock desaggregation and sample prepartion techniques used in the different laboratories. However, in order to enable interpretation of our results regarding white K-mica polytype transformation as a function of grade, the IC data obtained during the course of these investigations plus additional metamorphic indicators described in the literature were used.

The variation of IC within a single outcrop may be evaluated from table 2. The following pairs of samples show only a small variation in IC values when measurements from the same laboratory are compared: N78-47A and N78-47B, Z75-40C and Z75-40D, NZ4 and MF2839, as well as NZ9 and MF2848. A relatively large variation in IC values obtained in this study was found between samples NZ8 and MF2846 and may be due to peak broadening in sample NZ8 caused by increased mechanical grinding using a small sample size.

Ad, 1Md, 1M, AND $2M_1$ STRUCTURES

The percentage of $2M_1$ is obtained from the $2M_1/(2M_1 + 1M)$ ratio (see Tab. 2) and from figure 2. The calibration curve obtained in this study is similar to that provided by DALLA TORRE et al. (1994) and its quality may be estimated using the criterion suggested by these authors. They formulated an intensity factor written as $v = w_p(1-r)/r(1-w_p)$, where w_p is the weight fraction of $2M_1$ in the mixture and r is the ratio $2M_1/(2M_1+1M)$ obtained from the measurements. According to DALLA TORRE et al. (1994), v should be constant for every combination of w_p and r. In the present study, we found that v is relatively constant in a range from 10 to 80% $2M_1$ polytype in the mixture. Outside this range, v displays a larger variation owing to the small amounts of $2M_1$ and 1M polytype in the mixture. This observation results in the fact that estimates of $\%2M_1$ outside this range ($2M_1/(2M_1+1M) < 0.15$ and > 0.7) display a larger uncertainty than those within this range. However, DALLA TORRE et al. (1994) estimated that the absolute error of the method lies around ± 2% for a mixture containing equal proportions of both polytypes (see also below).

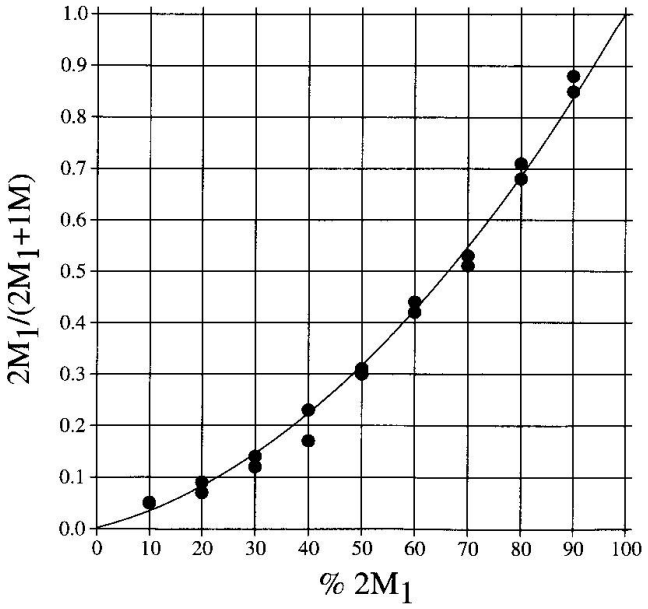


Fig. 2 Calibration curve of $\%2M_1$ versus $2M_1/(1M + 2M_1)$ used in this study.

It has been agreed that IC is primarily a function of temperature and improves with increasing metamorphic grade (e.g., FREY, 1987). This statement is also true for the samples investigated here: IC values decrease with improving vitrinite reflectance in the Dachschiefer and increasing grade as determined by metamorphic mineral assemblages in the New Zealand samples (KISCH, 1980b; WARR, 1996). Moreover, chemical, XRPD, infrared, and petrological data from the Keuper and Quartenschiefer samples (HUNZIKER et al., 1986) as well as additional XRPD and petrological data from the Jämtland, SW England, and ILC samples (see KISCH, 1980a; WARR and RICE, 1994; S. Krumm, written comm., 1995) support this general trend. For these reasons, improving IC can be interpreted to reflect increasing metamorphic conditions, and it is therefore appropriate to correlate IC values with estimates of the amount of $2M_1$ in a sample.

Plots of $\%2M_1$ versus IC for the various sample groups studied are shown in figure 3. Samples that contain disordered white K-mica structures were not considered in these plots because the amount of $2M_1$ can quantitatively not be determined (see above). In general, the data show that 100% $2M_1$ is reached at the onset of the epizone, a few exceptions excluded (see Tab. 2). Three anchizonal samples (MF131, MF703, and MF71) also contain 100% $2M_1$. Except for the SW samples, the relationship between $\%2M_1$ and IC is not that obvious and correlation coefficients are generally small. However, the plots reveal that increasing $2M_1$ contents are related to decreasing IC values, i.e. increasing grade. This is even more evident if samples that contain disordered structures, established on the basis of an elevated background in XRPD patterns, are considered. Inspection of table 2 reveals that disordered poly-

types prevail in samples belonging to the diagenetic zone. XRPD patterns of almost all of these samples reveal weak and diffuse 1M [112] and $2M_1$ [025] reflections indicating that a mixture of 1M and $2M_1$ is associated with a disordered polytype. XRPD patterns of ethylene glycolated preparates containing a mixture of 1M and $2M_1$ associated with disordered structures showed better resolved diagnostic ordered polytype reflections for a few samples only. No effect upon glycolation was observed for the majority of the preparates, indicating larger amounts of disordered structures than mixtures of ordered polytypes. The XRPD patterns of samples L10 and F176 show weak $2M_1$ [025] and no 1M [112] reflections upon glycolation (see Fig. 4a for diagenetic sample L10 – for comparison sample MF52 with a $2M_1/(2M_1+1M)$ ratio of 0.61 is shown in Fig. 4b). Using the criterion for the definition of the 1Md polytype (absence of diagnostic 1M reflec-

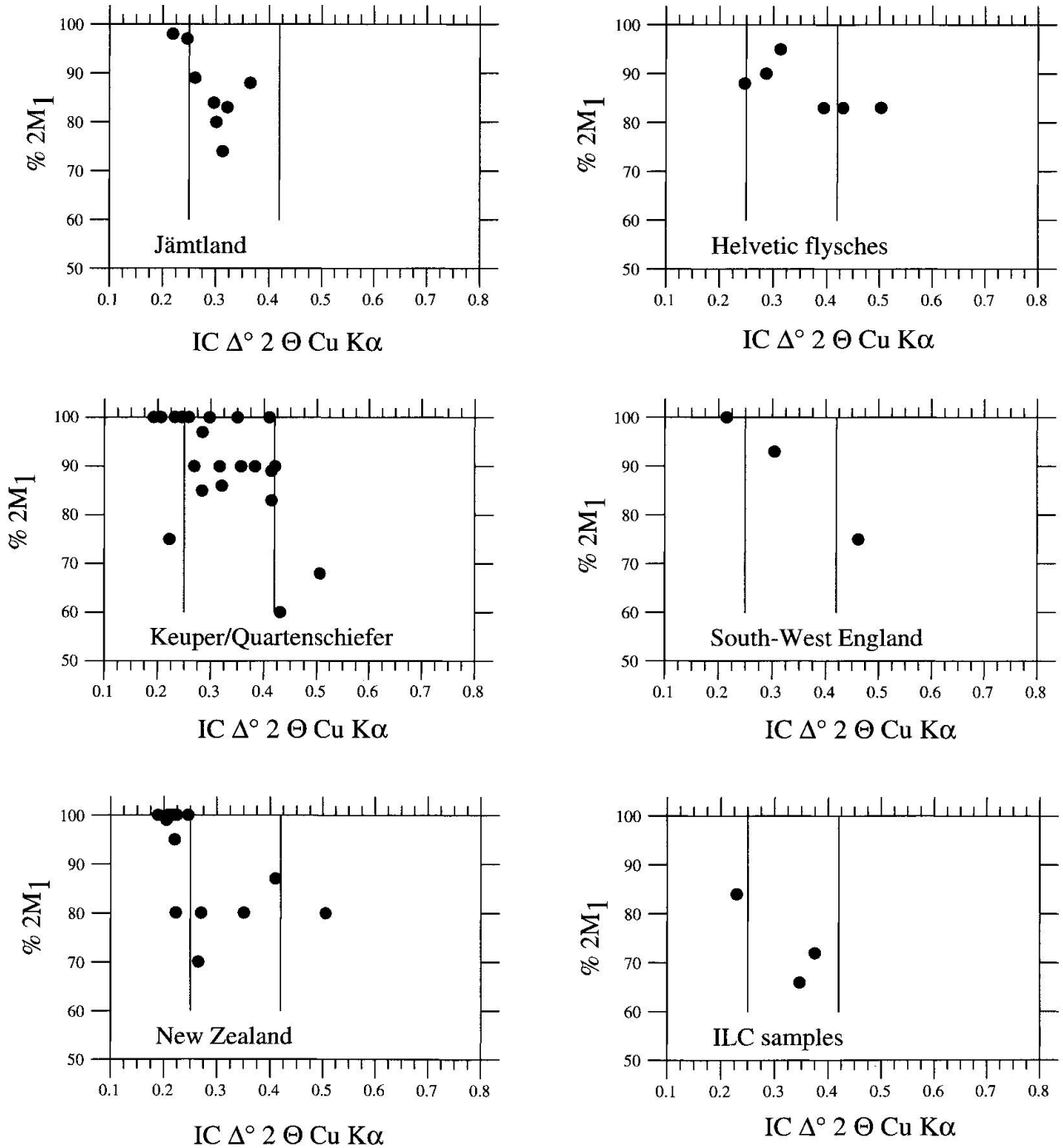


Fig. 3 % $2M_1$ versus illite crystallinity (IC) data for the various sample groups studied. Solid lines between 0.25° and 0.42° Δ2Θ CuKα indicate the IC limits of the anchizone.

tions with $k \neq 3n$ in addition to the elevated background), this observation may indicate that both samples contain large proportions of 1Md and only a small amount of $2M_1$ structures.

In summary, our results show that according to the criteria for the definition of different polytypes most of the diagenetic samples, except samples L10 and F176, contain large amounts of disordered group A white K-micas and small amounts of a mixture composed of 1M and $2M_1$. These observations suggest that the low-grade diagenetic samples are generally free of 1Md structures and that the true 1Md structure is far less abundant than previously suggested (e.g., VELDE and HOWER, 1963). Moreover, our data also indicate that the 1M structure is not a very common form of white K-mica polytypes. The $2M_1$ structure prevails in most samples free of disorderd white K-mica. The largest concentrations of 1M is around 40% (sample MF23). Our observations are generally consistent with results presented by AUSTIN et al. (1989). Based on a XRPD study of K-bentonites, which are entirely diagenetic in origin, these autors found that Ad and mixtures of 1M and $2M_1$ structures are the dominant polytype forms, whereas the 1Md structure is relatively rare.

The reproducibility of the method as well as the variation in the content of a specific polytype within an individual outcrop may be estimated from table 2. As previously mentioned, there are five pairs of samples each of which was collected from the same outcrop. The variation in $\%2M_1$ for most of these samples is ± 2% or smaller (N78-47A and N78-47B, Z75-40C and Z75-40D, NZ4 and MF2839, NZ8 and MF2846). For the pair of samples NZ9 and MF2848, the variation is of the order of ± 4%. These observations suggest that the method proposed by DALLA TORRE et al. (1994) is capable to estimate relative proportions of 1M and $2M_1$ in samples free of disordered white K-mica structures with a fairly high degree of reliability. Moreover, individual outcrops appear to be homogeneous with respect to a specific polytype concentration.

BRINDLEY (1980) as well as SRODON and EBERL (1984) suggested that 1Md structures may exist only if smectite is interlayered with white K-mica. AUSTIN et al. (1989), however, found that smectite interstratification is not a necessary condition for the presence of a disorderd polytype. During the course of this study, disordered structures were observed in 14 samples, 12 of which contain mixed-layer illite/smectite. This observation suggests that the presence of smectite interstratification favours disorder in white K-mica.

EVOLUTION OF WHITE K-MICA POLYTYPES AS A FUNCTION OF TEMPERATURE

In the laboratory, YODER and EUGSTER (1955), VELDE (1965), and MUKHAMET-GALEYEV et al. (1986) have found that the 1Md –> 1M –> $2M_1$ white K-mica polytype transformation is a function of temperature. Also on a regional scale many workers found that increasing amounts of $2M_1$ are related to an increase in metamorphic grade in terms of temperature (for references, see DALLA TORRE et al., 1994; RUIZ CRUZ and ANDREO, 1996). A literature compilation by FREY (1987) showed that the conversion from 1Md towards

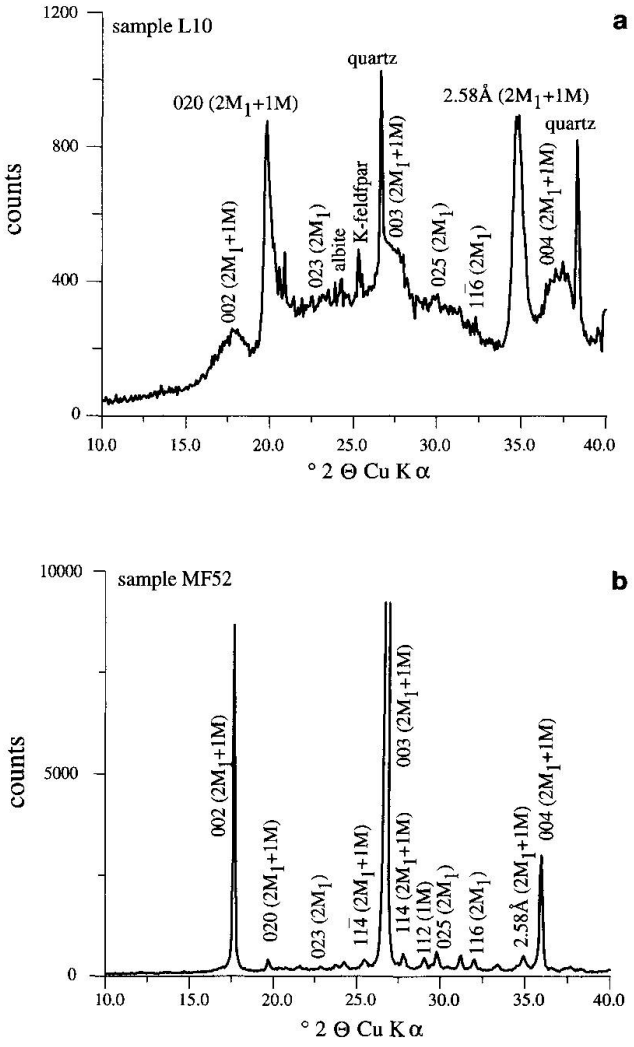


Fig. 4 (a) X-ray powder diffraction pattern of sample L10 after 128 hours in glycolated atmosphere. The elevated background between 20° and 33° 2Θ CuKα is clearly visible. No 1M [112] peak can be detected, however, a weak $2M_1$ [025] reflection does occur. For further details see text. (b) X-ray powder diffraction pattern of sample MF52 showing discrete 1M [112] and $2M_1$ [025] reflections in addition to a low background and well resolved 00*l* peaks.

$2M_1$ is completed at approximately the anchizone/epizone boundary. These previous studies based the evaluation of the relative amount of $2M_1$ versus 1Md or 1M on criteria developed by YODER and EUGSTER (1955) and LEVINSON (1955) or on methods that used different peak intensity ratios (VELDE and HOWER, 1963; REYNOLDS, 1963; MAXWELL and HOWER, 1967). However, two recent studies (AUSTIN et al., 1989; DALLA TORRE et al., 1994) showed that the criteria to distinguish between Ad, 1Md, 1M, and $2M_1$ used in this study are more useful than the ones presented in earlier studies. On the basis of these criteria our data suggest that in the diagenetic zone Ad structures prevail and are transformed into mixtures of 1M and $2M_1$ structures in the anchizone. As grade increases, the amount of 1M polytype decreases in favour of $2M_1$ structures until, at epizonal grades, all 1M is converted to $2M_1$ structures.

Conclusions

Based on methods developed by previous researchers, many workers concluded that 1Md is a common structure of illite in sedimentary rocks under diagenetic conditions. A recent study by AUSTIN et al. (1989) proposed, however, based on new criteria to differentiate between 1Md and Ad structures, that 1Md is less common than previously suggested. The data obtained in this study are consistent with their observations. At diagenetic grade, newly formed white K-mica crystals generally exhibit disorder. In most cases, these structures belong to the disordered group A micas (Ad) according to the terminology by BAILEY (1988) and AUSTIN et al. (1989). At diagenetic grades, Ad structures prevail and are associated with small amounts of mixtures of 1M and $2M_1$ polytypes. Our study further suggests that disorder in white K-mica is favoured by the presence of smectite interstratifications. Disordered structures do not occur at anchizonal grades, but a mixture of 1M and $2M_1$ white K-mica polytype with larger proportions of the latter prevails. 90% of the anchizonal samples studied exhibit $2M_1$ concentrations that cover the range from 70 to 90%. At the onset of the epizone, 100% $2M_1$ are generally reached, although there are a few exceptions to this rule. At IC values smaller than 0.2° $\Delta 2\Theta$ CuKα, 1M structures were not found in any of the samples studied. The 1M polytype generally appears to be less common than the $2M_1$ structure, even at lower grades. The results obtained in this study show that with improving illite crystallinities, white K-mica crystals evolve from Ad structures in the diagenetic zone to a mixture of 1M and $2M_1$ with variable but larger proportion of the latter in the anchizone to 100% $2M_1$ in the epizone. Thus, determination of white K-mica polytypes appears to be a useful indicator to determine the grade of metamorphism of sedimentary rocks metamorphosed at low-temperature conditions.

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