Conditions and Timing of Pumpellyite– Actinolite-facies Metamorphism in the Early Mesozoic Frontal Accretionary Prism of the Madre de Dios Archipelago (Latitude 50°20'S; Southern Chile)

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The Madre de Dios Metamorphic Complex (MDMC) in southern Chile is a fossil frontal accretionary prism, which is mainly composed of metapsammopelitic rocks, intercalations of oceanic rocks (greenstone and metachert) and platform carbonate. We concentrated on the metabasite to decipher the metamorphic evolution. This rock type contains assemblages of the pumpellyite-actinolite facies: $pumpellyite \pm actinolite-chlorite \pm grandite \pm phengite \pm epidote$ albite-quartz-titanite $\pm K$ -feldspar \pm calcite. The metamorphic phases mainly grew by prograde hydration reactions during various episodes of restricted fluid influx. Fundamental phase relations of the pumpellyite-actinolite facies and adjacent facies were reproduced by pseudosections calculated for the system $K_2O-Na_2O-CaO FeO-O_2-MgO-Al_2O_3-TiO_2-SiO_2-H_2O-CO_2$ at 200-400°C and 1–9 kbar. The calculated stability fields of the metamorphic assemblages as realized in the MDMC metabasite indicate highest metamorphic conditions restricted to 290-310°C, 4-6 kbar for the MDMC, presumably as a result of the main fluid influx at these conditions. Nevertheless, earlier local equilibria are still preserved as a result of strongly kinetically controlled mineral reactions and a lack of recrystallization and compositional homogenization at thin-section

scale. Hence, thermodynamic calculations of local multivariant mineral equilibria using the entire compositional variation of minerals in the MDMC show that the prograde PT path evolved from 4 ± 1 kbar, $200-220^{\circ}C$ to 5 ± 1 kbar, $290-330^{\circ}C$. The prograde PT path reflects nearly horizontal particle paths after reaching the maximum depth typical for frontal accretionary prisms. Long residence at maximum depth resulted in thermal re-equilibration. ${}^{40}Ar/{}^{39}Ar$ spot ages were measured by in situ UV laser ablation of local phengite concentrations in a deformed metapelite at $233 \cdot 2 \pm 1 \cdot 8$ Ma and in an undeformed metabasite at 200.8 ± 2.4 Ma. Whereas the first age represents an age of accretion, the latter age can be attributed to mineral growth either during a younger stage of accretion or during a retrograde stage. ⁴⁰Ar/³⁹Ar isotopic analyses of two further metabasite samples reflect a prominent resetting of ages at 152.0 ± 2.2 Ma and white mica growth during external fluid access triggered by either a local intrusion or a late Jurassic extensional episode.

KEY WORDS: pumpellyite-actinolite facies; kinetically controlled mineral growth; frontal accretionary prism; prograde PT path; PT pseudosection; 40Ar/39Ar UV laser ablation

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INTRODUCTION

The Patagonian Pacific margin between latitudes 42°S and 53°S is characterized by numerous Late Paleozoic-Mesozoic metamorphic complexes, which are generally referred to as fossil accretionary prisms (Hervé et al., 2003, 2007b; Fig. 1). These complexes vary in metamorphic grade, tectonic style, and age of metamorphism and accretion. The different basement complexes are generally separated from each other by the intrusion of the Late Jurassic to Cenozoic Patagonian Batholith (Hervé et al., 2007a, 2007b). Recent data have resulted in a better understanding of the formation of different types of accretionary prisms at the western margin of Gondwana. Two principal modes of accretion have been recognized in central Chile by Richter et al. (2007). Frontal accretion, involving subhorizontal convergence at shallow levels, changed in time to basal accretion involving underplating and subvertical flattening at deeper levels. In Patagonia such continuous relations can also be observed in basement rocks of the

Chonos Archipelago (Davidson et al., 1987; Willner et al., 2000). The different modes of accretion are also reflected by specific metamorphic conditions in the Chilean fossil accretionary systems. Basal accretion is clearly related to high-pressure (HP) greenschist-facies and more rarely to epidote-blueschist- and albite-amphibolite-facies conditions (Willner et al., 2000, 2004; Willner, 2005). However, areas showing frontal accretion are mostly overprinted by later high-temperature (HP), low-pressure (LP) metamorphism in central Chile (Willner, 2005). In Patagonia there are three major basement complexes, which are characterized by very low grade metamorphism, intermediate pressure conditions and an upper crustal deformation style that resembles that of frontal accretion, involving subvertical folds and brittle reverse faulting. These complexes comprise the Eastern Belt of the Chonos Archipelago (Willner et al., 2000; Fig. 1), the Eastern Andean Metamorphic Complex (Ramírez Sánchez et al., 2005) and the Madre de Dios Metamorphic Complex (MDMC; Thomson &



Fig. 1. Geological map and cross-section of the MDMC in the southern Madre de Dios Island and northern Duque de York Island of the Madre de Dios Archipelago after Forsythe & Mpodozis (1983) and Sepúlveda et al. (2008). Insert map shows the distribution of metamorphic complexes in Chilean Patagonia.

Hervé, 2002; Sepúlveda *et al.*, 2008). Such types of accretionary prism are, in general, predominantly composed of monotonous turbiditic successions. However, in the MDMC considerable amounts of oceanic crust and platform carbonate are also incorporated.

Focusing on the well-exposed MDMC, our aim is (1) to provide quantitative data for the thermal evolution of this example of a frontal accretionary prism using mainly metabasite as the lithology with the most variable assemblages, (2) to understand the nature of the low-temperature metamorphic reaction processes, (3) to apply new methods to study fundamental phase relations and metamorphic processes at very low grade conditions and (4) to date the very low grade metamorphic event so as to set an important time horizon for the evolution of the coastal accretionary systems of Chile as a whole.

GEOLOGICAL SETTING AND FIELD RELATIONS

The MDMC is an isolated complex of metamorphic rocks in the Ultima Esperanza District of Chilean Patagonia between latitudes and longitudes of 50 and 53°S and 74 and 76°W, respectively, and is exposed on various remote islands (Mornington, Madre de Dios, Duque de York, Diego de Almagro, Ramírez, Contreras and Desolación Islands) along the Pacific margin. During their pioneering work, Forsythe & Mpodozis (1979, 1983) defined three units of the MDMC that are composed of distinct rock assemblages (Fig. 1): (1) the Denaro Unit (DU) is composed of large fragments of ocean floor rocks and their sedimentary cover (metalliferous chert, redeposited calcareous sandstone, black shale and banded radiolarian chert with a Late Carboniferous-Early Permian biostratigraphic age; see Ling et al., 1985). The metabasite of the DU shows geochemical affinities to enriched (E-) and normal (N-) mid-ocean ridge basalt (MORB) (Sepúlveda et al. 2008), whereas the metalliferous chert is comparable with exhalative precipitates at active spreading centers. Primary structures such as pillow and hyaloclastite relics are preserved and, generally, no internal deformation of the rocks is observed. (2) The Tarlton Limestone (TL) represents a marine carbonate platform of Middle Pennsylvanian to Early Permian age (Cecioni, 1956; Douglass & Nestell, 1976). (3) The Duque de York Unit (DYU) is the predominant unit and comprises a voluminous turbiditic metapsammopelitic succession of continental provenance, which also includes polymict conglomerates. The DYU was partly unconformably deposited on top of the DU and TL units, but is mostly in tectonic contact with its neighbouring units. A combination of the palynological record and geochronological data for the DYU suggests an earliest Middle Permian depositional age (Sepúlveda et al., 2009). Sensitive high-resolution ion microprobe (SHRIMP) U-Pb dating of detrital zircon from DYU metagreywacke yielded a youngest age population of c. 270 Ma that provides a maximum depositional age for the sequence (Hervé et al., 2003, 2006). These data also provide an uppermost limit for the age of metamorphism. Two fission-track (FT) ages were obtained from the same detrital zircon populations: 209 ± 14 and 209 ± 12 Ma (Thomson & Hervé, 2002). Considering annealing of zircon FT ages at $\sim 280^{\circ}$ C for mean cooling rates (Rahn et al., 2004) the latter ages provide a minimum age of metamorphism. The DYU is regarded to have been deposited at an active continental margin on the basis of the composition of the detritus (Faúndez et al., 2002; Hervé et al., 2003; Lacassie et al., 2006). A prominent Early to Middle Permian (c. 270 Ma) population of detrital zircon in the DYU can be interpreted as the first input of detritus from an igneous complex that developed within the continental margin at this latitude (Hervé et al., 2003, 2006). However, such source rocks are apparently not exposed at the present margin of Southern Patagonia at the respective latitude. Thus, Lacassie et al. (2006) suggested that the MDMC may have been displaced and possibly originated at an extensive late Paleozoic active continental margin along the Antarctic sector of Gondwana. On the other hand, the late Permian zircon population might correspond to the widespread Permian(?)-Triassic Choiyoi acid magmatic province (Mpodozis & Kay, 1990) that extends from 28°S to 42°S, or to the Permian igneous rocks in the North Patagonian Massif (Pankhurst et al., 2006).

The MDMC was previously classified by Forsythe (1982) and Forsythe & Mpodozis (1983) as a forearc accretionary prism. Those workers described the predominant structures as follows: east-west-trending thrusts dipping north (D_1) were produced during north-to-south-directed (relative to present coordinates) tectonic emplacement of slices of the oceanic DU and TL within the continent-derived DYU. At the same time similarly trending tight to isoclinal folds formed as well as an early cleavage in the metapelitic rocks. Primary structures are generally preserved and no internal deformation occurs in the metagreywacke, metabasite and massive limestone. D_1 structures were strongly overprinted during north-south-trending refolding with a prominent 1-100 m scale, slightly west-vergent chevron folds and associated axial plane cleavage in pelitic rocks. These D_2 structures were thought to be related to a system of strike-slip faults. The prominent bedding folds and associated thrusts resemble structures formed during frontal accretion in shallow levels of an accretionary system as observed in analog experiments (Kukowski et al., 2002; Glodny et al., 2005) and rock units such as the Eastern Series of central Chile (Richter et al., 2007), which are interpreted in a similar fashion to a frontal accretionary prism.

After emplacement and development of a structural inventory, the units of the MDMC were intruded by the late Jurassic to Cenozoic South Patagonian Batholith (Hervé *et al.*, 2007*a*). In the study area this intrusion occurred at 133 ± 1 Ma (Hervé *et al.*, 2007*a*). Late Jurassic silicic volcanic rocks of the Tobífera series represent the oldest cover sequence in the area, and unconformably overlie the metamorphic basement at Peninsula Staines (51°33'S; Allen, 1982).

Rapalini *et al.* (2001) provided paleomagnetic data on the TL and the DU, which suggest that both units rotated $\sim 117^{\circ}$ in an anti-clockwise sense after an Early Cretaceous remagnetization caused by the thermal influence of the South Patagonian Batholith. Those workers concluded that both rock units were probably accreted to the Gondwana margin from the NW.

ANALYTICAL METHODS

Focusing on the lithologically most diverse Denaro Unit (DU), we selected representative rock types from different parts of its accessible outcrop (Fig. 1) for petrological and geochronological investigations. The mineralogy of the rock samples and their locations are given in Table 1.

Mineral compositions were obtained using a CAMECA SX 100 electron microprobe with five wavelengthdispersive systems at Universität Stuttgart, Germany. Operating conditions were an acceleration voltage of 15 kV, a beam current of 15 nA, 20 s counting time per element each on the peak and the background and a defocused beam of 8 µm to avoid loss of alkalis in mica and amphibole. We used natural minerals, glasses and pure oxides as standards. The PAP correction procedure provided by Cameca was used for matrix correction. Representative analyses and structural formulae of minerals used for PT calculations, together with the calculation procedure of the structural formulae, are presented in Table 2. The complete dataset is available as Supplementary Data, which can be downloaded from http://www.petrology.oxfordjournals.org. Abbreviations of minerals and end-member components in this paper are: ab, albite; ac, Mg-Al-celadonite; am, amphibole; bt, biotite; ca, calcic amphibole; cc, calcite; ch, chlorite; cl, clinochlore; cp, clinopyroxene; cz, clinozoisite; da, daphnite; ep, epidote; fc, Fe-Al-celadonite; gl, glaucophane; gt, grandite; kf, potassic feldspar; lm, laumontite; lw, lawsonite; mp, Mg-pumpellyite; na, sodic amphibole; pu, pumpellyite; pr, prehnite; qz, quartz; sb, stilbite; st, stilpnomelane; tt, titanite; tr, tremolite; v, H₂O vapor; wk, wairakite; wm, potassic white mica.

Whole-rock major element analyses were obtained using Philips X-ray fluorescence spectrometers on glass disks at Ruhr-Universität Bochum and Universidad de Chile in Santiago. FeO was determined potentiometrically and Fe₂O₃ was calculated by difference (Fe₂O₃tot -FeO*1·1113). H₂O was analysed by the coulometric Karl-Fischer titration method. Data are presented in Table 3.

Table 1: Assemblages of rock samples and their locations

	M	etar	norp	ohic	pha	ses							Amy	gdules	Prim	ary ph	ases	Latitude	Longitude	Location	Ar/Ar age	Pseudo-	Multivariant
	Ad	G G	t Pi	и Ер	Ch	Wm	ו Kf	Ab	Qz	Ti	Cc	St			Срх	Cr-sp	Plag				(IVIA)	section	reactions
Metabasite																							
04CH18c	х		х	x	x	х		x	x	х			Ch,	Qz, Ep	x		х	50°27′57·9″	75°12′19·8″	Isla Denaro	207-136	x	x
04CH17c					x	х		х	x	х			Ch		х		x	50°28′10·6″	75°11′59·7″	Isla Denaro	152 ± 2		
MD98-03		х	х	х	x			х	х	х					х	x		50°18′48·2″	75°16′50·3″	Seno Eleuterio			
MD98-04	x	х	х	х	x	х	х	х	x	х					х	x		50°18′48·2″	75°16′50·3″	Seno Eleuterio		x	x
MD06-5B	x	х		х	x	х		х	x	х	x		Qz,	Ch, Co	x	x		50°18′52·40″	75°16′50·57″	Seno Eleuterio			x
MD5	x		х	х	x	х		х	x	х	x		Ch,	Qz	х			50°28'36·4″	75°11′33∙5″	Islotes Roncas		x	x
MD06-6A	х				х			х		х	x		Ch,	Сс	х			50°18′52·40″	75°16′50·57″	Seno Eleuterio			
MD26	х		х	х	x	х		х	х	х	x		Ch,	Сс	х			50°22′42·1″	75°22′58·6″	Seno Eleuterio		x	x
MD05-18			х	х	x		х	х	x	х								50°23′31·7″	75°20′10·1″	Isla Guarello			
MD05-11D				х	х	х		х	x	х	x		Qz,	Ch, Co	x			50°22′31.0″	75°22′46·9″	Seno Eleuterio	$201\pm\!2$		
MD06-3B			х	х	х	х	х		x	х					х			50°22′44·67″	75°23′05·63″	Seno Eleuterio		x	
SLL853*	x		х	х	x	х		х	x	х		x			х			45°20′56·1″	74°12′05·7″	Isla Italia		x	
Metapsamr	пор	oelit	е																				
04CH15					х	х		х	x		x							50°25′43·2″	75°19′33·1″	Isla Madre de Dios	233 ± 3	x	
MD06-8					x	x	х	x	x	х								50°17′41·41″	75°20′25·03″	Isla Madre de Dios		x	

*Metabasite from the Chonos Archipelago (Hervé et al. 1999).

Table 2: Representative analyses of the peak metamorphic mineral compositions

	Garnet					White mic	а										
	MD9803	MD065B	MD9804	MD9804		MD9804	MD9804	MD26	MD26	04CH18c	04CH18c	MD5	MD068	04CH15	04CH17c	MD0511D	MD065B
SiO ₂	35.8	36.1	35.9	calc.	SiO ₂	55.3	calc.	49.4	calc.	49·1	calc.	calc.	50.4	51.6	50·3	52.7	50.3
Al ₂ O ₃	8·11	6·15	6.39		TiO ₂	0-01		0.03		b.d.			0·14	0.03	0.04	0.02	0.52
TiO ₂	0·38	0.42	06.0		Al ₂ O ₃	21.7		28·0		27·3			27·2	26.7	26·8	24.7	24.1
Fe ₂ 0 ₃	20·1	22·1	19-4		FeO	3.91		3·04		4.60			3·01	2.54	3·84	3·20	4.53
Cr ₂ O ₃	0.03	n.d.	1.69		Fe ₂ 0 ₃												0.13
MnO	0.21	0.25	0.40		MnO	0.03		0.02		0.01			b.d.	0.04	0.02	b.d.	0.03
MgO	0.05	0.26	0·20		MgO	5.61		2.77		1.78			2.66	2.22	2·74	3·03	4.14
CaO	34.9	33.6	34·2		CaO	0.05		0.00		0.59			0.02	0.02	0.80	0·20	1.20
Sum	9.66	98·8	99·1		Na ₂ O	00.00		0·18		0.70			0.15	0.84	0.49	1.12	0.47
Si	5.850	5.966	5.920	6.00	K ₂ 0	10.5		10.9		9.8			10.3	9.8 8	9.4	9.6	10.2
Al∾	0.150	0.034	0.080		H ₂ 0	4.59		4.40		4.37			4.44	4.45	4.43	4-47	4.42
Sum	6·000	6.000	6.000	6.00	Sum	101·8		98·7		98·3			98·6	98.4	98·7	99·2	100.1
AI ^{VI}	1-412	1.165	1.160	1.36	Si	7·226	6.90	6·693	6·90	6·744	6·86	6·94	6·801	6·951	6·802	7.078	6·827
Fe ³⁺	2.470	2.747	2.402	2.64	AIV	0.774	1·10	1·308	1·10	1.256	1·14	1·06	1.199	1·049	1·198	0.922	1·174
Ξ	0.046	0.052	0·111		Sum	8·000	8·00	8·000	8·00	8·000	8·00	8·00	8·000	8·000	8·000	8·000	8·000
Ċ	0.004	n.d.	0·220		AI ^{VI}	2.574	3·10	3·158	3·10	3·157	3·14	3·06	3·132	3·187	3.069	2.994	2.679
Sum	3·929	3·964	3·893	4·00	Ξ	0.001		0.003					0·014	0.003	0·004	0.002	0.053
Mn	0.030	0.035	0.055		Fe ²⁺	0-427	0.10	0.345	0·22	0.528	0·26	0·30	0.339	0·286	0.434	0.360	0-514
Ca	6·114	5.946	6-041	6.00	Fe ³⁺												0.014
Mg	0.013	0.064	0.049		Mn									0.005	0·002	0.000	0.003
Sum	6·156	6.046	6·145	6·00	Mg	0.004	0·80	0.003	0·68	0.001	0.60	0·64	0.534	0-446	0.552	0.607	0·837
Grossular	0.401	0-454	0.391	0·34	Sum	1·094	4·00	0.558	4·00	0·363	4·00	4·00	4·020	3·928	4·061	3·963	4·100
Andradite	0.592	0.529	0.556	0.66	Са	4.099		4·067		4·049			0.003	0.003	0·116	0·028	0.175
Spessartine	0.005	0.006	00·0		Na	0.007	0.04	000.0	0.04	0.087	0.04	0.40	0.040	0·219	0·129	0·292	0·125
Pyrope	0.002	0-011	0.008		⊻	0.000	1·96	0.047	1·96	0·186	1·96	1·96	1·781	1 ·689	1·614	1.650	1·768
Uvarovite	0.001	n.d.	0.036		Sum	1.751	2·00	1·887	2·00	1·723	2·00	2·00	1·835	1.919	1·885	1·973	2·068
					НО	1·758	4·00	1.934	4·00	1·996	4·00	4·00	4·000	4·000	4·000	4·000	4·000
					X_{Mg}	0·720	0·89	0.620	0·76	0.400	0·70	0·68	0.610	0.610	0.560	0.630	0.620
					Muscovite	0·330		0.584		0.423			0-546	0.433	0·347	0.300	0.277
					Tri-oct. mica	0.050		0.035		0·025			0.010	0.036	0.031	0.019	0.050
					MgAI-celadonite	0-444		0·217		0·169			0.250	0·293	0.267	0·348	0.309
					FeAl-celadonite	0.173		0·134		0·246			0.159	0·188	0·210	0·206	0.190
					Paragonite	0.000		0.024		0.093			0·022	0·114	0.069	0·148	0.060
					Rest	0.004		0.006		0-044			0.029	0-015	0.000	0.033	0·229
																(cor	itinued)

	Chlorite															
	MD9804	MD9804	MD26	MD26	04CH18C	04CH18C	MD5	MD5	MD9803	MD068	04CH15	MD066	MD065B	04CH17C	MD0511D	MD0518
SiO ₂	32·3	calc.	28·0	calc.	29.1	calc.	26-91	calc.	29.4	25.3	27·3	31.6	33·7	30.5	31-4	29.5
Al ₂ O ₃	15·8		19.2		16·1		18·59		17·8	17-5	14.3	15-9	14.0	15.5	17·0	19.3
Ti0 ₂	0.06		0.01		0-03		0-01		0.02	2.58	1.61	b.d.	0-01	b.d.	b.d.	b.d.
FeO	13·3		18.6		25·8		24.55		17·3	32.3	31.0	13.9	13.5	22.2	11·3	11-9
MgO	26.2		20-4		15.5		16.75		22·1	ĿĿ	11·8	25.3	26·2	19.3	27.0	26.9
MnO	0.16		0·22		0.28		0.20		0.19	0.37	0.11	0.17	0.22	0.20	0.15	0.25
H_2O'	12·3		11.7		11:3		11·35		11·8	10.7	10.8	12·1	12·3	11.7	12·2	12·3
ЦК	100·2		98·2		98·1		98·35		98·7	96.4	97·0	0.66	6.66	99·3	99·1	100·2
Si	6·321	6.00	5.759	6.00	6.171	6.00	5.689	6.00	5.968	5.685	6-059	6·263	6.592	6·265	6·154	5.757
Al ^{i∨}	1.680	2.00	2·241	2·00	1·830	2.00	2.311	2.00	2·032	2.315	1.941	1.737	1·408	1.735	1.846	2·244
AI ^{VI}	1.959	2.00	2.409	2·00	2·203	2·00	2.321	2.00	2·218	2·309	1·802	1·988	1·824	2·024	2·084	2·194
⊨	0.008		0.002		0.004		0.001		0.003	0.435	0·268	0.000	0.002	0.000	0.000	0.000
Mn	0.027		3·199		0.050		0.036		0.033	0.071	0.020	0·028	0.036	0.035	0.024	0.041
Fe	2·182	2·24	0.038	3·76	4.585	4·38	4·341	4.50	2·932	6.069	5·744	2·311	2·208	3·813	1.855	1.945
Mg	7.646	7.76	6.258	6·24	4·914	4·91	5·278	5.50	6.677	2.572	3·913	7·488	7·633	5.903	7·872	7·821
Sum	11-822	12.00	11-906	12·00	11-757	12·00	11-977	12·00	11·863	11 ·456	11·748	11·815	11·703	11·775	11·835	12·001
НО	16.000	16·00	16-000	16·00	16·000	16·00	0.55	16·00	16·000	16·000	16·000	16·000	16·000	16·000	16·000	16·000
$X_{\rm Mg}$	0·78	0·78	0.66	0.62	0.51	0.56	0.55	0.55	0.695	0·298	0.405	0·764	0·776	0.608	0·814	0.801
															(60	ntinued)

Table 2: Continued

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	Amphibo	e						Epidote								
	MD5	MD5	MD065B	MD066	MD9804	MD26		MD26	MD26	04CH18c	04CH18c	MD5	MD5	MD0511D	MD0518	MD9804
SiO ₂	53.4	calc.	57.5	56.4	calc.	calc.	SiO_2	37·2	calc.	36.7	calc.	37.3	calc.	37.8	37·8	36.8
Al ₂ O ₃	0·48		0.52	0·70			TiO_2	0.13		60.0		00.0		0.01	0.10	0.02
TiO ₂	0.06		0.01	0·13			AI ₂ O ₃	23·1		23·5		21.9		22·2	23·8	20·8
Fe ₂ O ₃	1·85		1.41	0·32			Fe ₂ O ₃	13·3		13·3		14·8		14·3	12·1	14·8
FeO	14.0		6.60	7.73			Mn_2O_3	0·20		0.39		0.13		0.05	0.16	0.15
MgO	13·6		19-4	18.9			MgO	0.03		0.02		0.15		0.46	0.03	0.10
CaO	11.9		12.6	12.6			CaO	23·2		23·0		22.9		22.9	23·5	21·8
MnO	0.35		0.21	0.11			H_2O'	1.86		1·84		1.86		1·89	1·89	1·84
BaO	0.16		b.d.	0.03			Sum	99·1		98·7		99·1		9.66	99.4	96·4
Na ₂ O	0.06		0.01	0·08			Si	3·000	3·00	3·000	3·00	3·000	3·00	3·000	3·000	3·000
K ₂ 0	0·18		0·30	0.40			AI	2.196	2·36	2·265	2·40	2.075	2·36	2·074	2·220	1·995
H ₂ 0'	2·02		2.16	2.13			Fe ³⁺	0·804	0.64	0·817	0.60	0.895	0.64	0·851	0·725	0.910
Sum	98·1		100·8	99·5			Mn^{3+}	0.012		0.024		0.008		0.003	0.010	600·0
Si	7.915	8·00	7.968	7·951	8·00	8·00	Mg	0.003		0.002		0.019		0.055	0.004	0·012
AI ^{IV}	0·083		0.032	0.049			Ξ	0.008		0.005		000.0		0.001	0.006	0.001
Sum	7.998	8·00	8·000	8·000	8·00	8·00	Sum	3·022	3·00	3·113	3·00	2.996	3·00	2·983	2·964	2·927
AI ^{VI}	0.000	0.04	0.052	0.067	0.08	0.06	Ca	2·000	2·00	2·011	2·00	1.973	2.00	1.944	1.994	1·904
Ξ	0.007		0.001	0.013			НО	1.000	1·00	1·000	1·00	1.000	1·00	1.000	1·000	1.000
Mn	0.044		0.025	0.013												
Fe ³⁺	0·206	0.17	0·147	0·034												
Fe ²⁺	1.735	1.69	0.765	0.911	1.02	1-40										
Mg	3·011	3·10	4·010	3·963	3·90	3.54										
Sum	13·000	13·00	13·000	13·000	13·00	13·00										
Ca	1·893	1.80	1.875	1·898	1·88	1·84										
Ba	600·0			0.001												
Na	0.053	0.20	0.080	0·109	0·12	0·16										
×	0.012		0.001	0.014												
Sum	1.966	2·00	1·956	2·022	2·00	2.00										
НО	2·000	2·00	2·000	2·000	2·00	2·00										
$X_{ m tremolite}$	0.946		0.938	0.949												
$X_{glaucophane}$	0.000		0.016	0.034												
$X_{ m riebeckite}$	0.054		0.046	0.017												
X_{Mg}	0.600	0.65	0.811	0.806	0·79	0·72										

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(continued)

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Table 2: Continued

	Pumpellyite											Clinopyro	xene			
	04Ch18c	04Ch18c	MD9804	MD9804	MD5	MD5	MD26	MD26	MD9803	MD05-18		MD5	04CH18c	MD5	04CH17c	MD066
SiO_2	35-9	calc.	37.2	calc.	36-6	calc.	36.3	calc.	35.8	36.8	SiO ₂	50.7	51.5	50.7	53·2	52.4
TiO ₂	0.06		0.04		0.07		0.19		0.01	0.02	TiO_2	0.57	0.48	0-57	0·28	0.22
AI_2O_3	21.0		23·8		24.5		24.4		19-1	26.0	AI_2O_3	2.16	3·04	2.16	1·87	3·11
Fe ₂ O ₃	7·38		4·26		2.62		5.37		10-54	2.51	Fe_2O_3	1-51	1.15	1.51	1·33	1.37
FeO	3.46		0·32		2.77		1.62		2.72	0.57	FeO'	8·87	6.73	8·87	5.47	4.30
MnO	0.08		0.15		0.10		0.16		0.03	0·15	MnO	0·23	0.19	0.23	0·24	0.15
MgO	2.06		3·87		2.50		3·12		2.38	3·77	MgO	14.7	16.3	14·7	17-4	18·3
CaO	22:7		23·4		23·5		22·5		22·6	23·2	CaO	19.2	19·3	19·2	20.4	19·6
Na_2O	0.04		0.04		0.03		0.02		0-01	0.03	Na_2O	0·23	0.25	0·23	0·20	0·15
K_2O	b.d.		0.06		b.d.		0·06		b.d.	0-01	Sum	98·2	0.66	98·2	100-4	9.66
H_2O'	6.33		6.47		6.43		6-44		6·14	6-54						
Sum	0.66		9.66		99·2		100.1		99·4	9.66	Si	1.923	1.913	1·923	1.941	1.913
Si	5.948	6·00	6·034	6·00	5.985	6·00	5.915	6·00	6·114	5.911	AI	0-077	0.087	0-077	0.059	0.087
AI	4·111	4·74	4·544	4.96	4·713	4·72	4·688	4·76	3·854	4·920	Sum	2·000	2·000	2·000	2·000	2·000
F	0·008		0.005		600·0		0.024		0.002	0.002	AI ^{VI}	0.020	0.046	0-020	0.021	0.047
Fe ³⁺	0.920	0·26	0.520	0.04	0·322	0·38	0.659	0·24	1.355	0·303	F	0.016	0.013	0.016	0.008	0·00
Sum	5·039	5·00	5.068	5.00	5.044	5.00	5.370	5.00	5·210	5·226	Fe ³⁺	0.043	0·032	0.043	0.037	0·038
Mg	0.509	0.58	0.937	0.86	0.608	0.54	0.757	0.64	0.607	0.903	Fe ²⁺	0·283	0·209	0·283	0.167	0·131
Мn	0-011		0·020		0.014		0.022		0.005	0.020	Mn	0.007	0·00e	0.007	0.007	0.005
Fe ²⁺	0.480	0-40	0.043	0·14	0·379	0·36	0·221	0·36	0·388	0-077	Mg	0·833	906-0	0·833	0.949	0-997
Sum	1.000	1·00	1.000	1.00	1·000	1.00	1.000	1 ·00	1.000	1.000	Ca	0·781	0·770	0·780	0.796	0.766
Ca	4·035	4·00	4·074	4·00	4·113	4·00	3·923	4.00	4·132	3.985	Na	0.017	0·018	0-017	0-014	0-010
Na	0-012		0.013		0-010		0·00		0.004	0.008	Sum	2·000	2·000	2·000	2·000	2·000
\mathbf{r}			0·012				0.012			0.001						
Sum	4.047	4·00	4·099	4·00	4·127	4·00	3.941	4·00	4·136	3.995						
НО	7·000	7·00	7·000	7·00	7·000	7·00	7·000	7·00	7·000	7·000						
$X_{\rm Mg}$	0.510	0.59	0.980	0·86	0.620	0.60	0.780	0.64	0.610	0.920						
X_{Mg}^*	0·280	0-47	0.630	0·83	0.470	0-47	0.460	0.52	0·260	0.700						

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(continued)

Table 2: Continued

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Table 2: Continued

	Feldspar						
	MD26	MD9804	MD9804	04CH18c	MD5	MD0518	MD0518
SiO ₂	68·9	65·3	69·4	68·3	67·3	63·3	64·88
Al ₂ O ₃	19·5	19·5	20.3	19·5	19.2	19·6	17.84
TiO ₂	0.38	0.01	0.01	0.01	b.d.	b.d.	b.d.
FeO	0.26	0.11	0.02	0.26	0.36	1.75	0.29
MgO	0.56	0.01	b.d.	0.03	n.d.	2.88	0.01
MnO	0.04	0.01	b.d.	b.d.	n.d.	b.d.	0.01
CaO	0.76	b.d.	0.04	0.27	0.39	0.31	b.d.
BaO	n.d.	n.d.	n.d.	n.d.	b.d.	b.d.	0.40
Na ₂ O	10.8	0.06	10.9	11.3	11·5	10.8	0.07
K ₂ O	0.14	15·99	0.06	0.00	0.02	0.27	16·21
Sum	101.1	101·0	100.8	99·7	99.0	98.9	99.7
Si	2.981	2.977	2.992	2.993	2.979	2.844	3.015
Al ^{I∨}	0.019	0.023	0.008	0.007	0.022	0.156	0.000
Sum	3.000	3.000	3.000	3.000	3.000	3.000	3.015
Al ^{VI}	0.975	1.024	1.026	1.000	0.978	0.882	0.977
Fe	0.010	0.004	0.002	0.010	0.012	0.066	0.011
Mg	0.017			0.002		0.193	0.001
Mn	0.002						
Sum	1.016	1.029	1.029	1.012	0.990	1.142	0.990
Са	0.035		0.002	0.013	0.082	0.015	
Ва							0.007
Na	0.909	0.005	0.912	0.957	0.984	0.945	0.007
К	0.008	0.930	0.003	0.000	0.001	0.015	0.961
Sum	0.952	0.935	0.917	0.970	0.997	0.975	0.975
0′	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Albite	0.038	0.000	0.002	0.013	0.079	0.015	0.000
Anorthite	0.955	0.005	0.995	0.987	0.919	0.969	0.007
Orthoclase	0.008	0.995	0.004	0.000	0.001	0.016	0.986

calc., calculated with PERPLE_X (at 300°C, 5.6 kbar); b.d., below detection limit; n.d., not determined. For garnet, cations are based on 48 negative charges, including 10 cations in the tetrahedral and octahedral site to calculate Fe^{3+} . For white mica, the proportion of cations is based on 42 negative charges neglecting the interlayer cations; the sum of octahedrally coordinated cations is set at 4.1 to allow for an estimation of Fe^{3+} . For chlorite, cations are based on 56 negative charges; H_2O is calculated on the basis of OH = 16. For amphibole, proportion of cations is based on the sum of cations = 13, except for Ca, Na and K for estimation of Fe^{3+} , and on 46 negative charges. For epidote, proportion of cations is based on the sais of OH = 4; estimation of Fe^{2+} by assuming the X-position filled with divalent cations. For clinopyroxene, normalization to four cations is used to calculate Fe^{3+} . For feldspar, normalization is on the basis of 16 negative charges.

*Calculated with Fetotal.

Preparation and measurements for determination of the Kübler Index of white mica were carried out at the Universidad de Chile in Santiago. The <2 μ m fraction of pelitic rocks was separated using a HERMLE centrifuge and measured with a SIEMENS D5000 X-ray powder diffractometer using quartz as a standard, Cu K α radiation and automatic primary as well as secondary divergence

slits. Operating conditions were 40 kV acceleration voltage and 30 mA current. Each specimen was scanned from 2 to $23^{\circ}2\theta$ in steps of $0.02^{\circ}2\theta$ and an integration time of 5 s. Peaks were analyzed using the EVA software provided by SIEMENS.

 $^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$ dating was performed in the $^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$ geochronology laboratory at the Universität Potsdam after JOURNAL OF PETROLOGY VOLUME 00 NUMBER 0 MONTH 2009

Table 3: Whole-rock analyses and simplified compositions (also corrected for clinopyroxene content) used for the calculation of pseudosections (Figs 6–9)

	Whole-roo	k analyses	6							Simplified	compositi	ons			
Sample:	04CH18A	MD9804	MD063B	MD26	MD5	SLL853	MD066	MD0511D		04CH18A	MD9804	MD063B	MD26	MD5	SLL853
SiO ₂	48·1	45·8	47·9	50·5	47·2	49·0	43·5	43·4	SiO ₂	47·4	45·9	48·3	50·5	46·6	49·0
TiO ₂	1.01	0.53	0.64	1.10	0.96	1.16	0.57	0.53	TiO ₂	1.17	0.53	0.65	1.14	1.12	1.23
AI_2O_3	13·6	14·5	16·1	13.4	14.4	14·2	15·6	16·7	AI_2O_3	16.3	14·5	16·2	13·9	19·2	15·7
FeO	7·91	6.56	4.60	6.48	6.80	9.56	8.48	8·52	$\rm FeO_{tot}$	11.7	9·15	8·75	9·71	8.04	11·5
Fe ₂ O ₃	3.25	2.85	4·52	3.34	3.30	1.74	0.96	4.00	MgO	8·14	16·6	8.04	9.39	5·77	4.49
MgO	9.60	16.49	7·97	9.78	8·13	5.49	15·16	7.39	CaO	5.53	3.29	5.95	7·51	9.90	10.1
MnO	0.16	0.14	0.09	n.d.	0.16	0.17	0.13	0.10	Na ₂ O	3·27	0.91	2·21	1.91	3.73	3.64
CaO	8·24	3.28	5.90	8·11	12·3	10.9	1.49	7.04	K ₂ 0	0.36	0.68	2.26	0.18	0.12	0.06
Na ₂ O	2.72	0.91	2·19	1.82	2·75	3.28	2.65	3.07	H_2O	5·97	8·15	6.96	5.06	5.19	4·21
K ₂ 0	0.29	0.68	2·24	0.17	0.09	0.05	0.23	1·57	CO ₂	0.00	0.00	0.45	0·53*	0.14*	0.00
$P_{2}O_{5}$	0.06	0.09	0.22	n.d.	0.10	0.21	0.08	0.25	0 ₂ †	0.15	0·15	0.15	0.15	0.15	0.15
H ₂ O/LOI	4·74	8·13‡	6·90‡	5·30‡	3·84‡	3·77‡	9.67	7·20‡		100.0	100.0	100.0	100.0	100.0	100.0
CO ₂	0.00	n.d.	0.45	n.d.	n.d.	n.d.	0.39	n.d.							
Sum	99.6	99.9	99.8	100.0	96.3	99.6	98·6	99·7							
FeO _{tot}	10.8	9·13	8·67	9.49	9.77	11.1	9.34	12·1							
Cpx§	0.22	0.00	0.00	0.05	0.27	0.10	0.00	0.00							

SLL853 is a metabasite from the Chonos Archipelago (Hervé et al., 1999). n.d., not determined.

*CO₂ estimated according to calcite content in the rock.

[†]Content of O₂ used for calculation.

‡Loss on ignition.

Scontent of clinopyroxene as a fraction of 1.

neutron activation of polished sections (1 cm diameter) at the Geesthacht Neutron Facility (GeNF) of the GKSS in Geesthacht, Germany. The polished thick sections were wrapped in commercial Al foils and set into a 99.999% pure Al holder of 20 mm diameter and 88 mm height consisting of 18 stacked Al disks. The package was Cd-shielded and irradiated with fast neutrons with a flux of 1×10^{12} n/cm²/s for 97 h. The Fish Canyon Tuff sanidine (age 27.5 Ma; Uto et al., 1997; Ishizuka et al., 2002) was used as a flux monitor during irradiation to obtain the I values, which reflect the degree of neutron activation for the irradiated samples. K₂SO₄ and CaF₂ crystals were also irradiated to correct interference of Ar isotopes produced by the reactions on K or Ca in the samples. The Ar isotopic analytical system at Universität Potsdam consists of (1) a New Wave Gantry Dual Wave laser ablation system with a 50 W CO_2 laser (wavelength 10.6 µm) and 6 mJ UV pulse laser (wavelength 266 nm, frequency-quadrupled) for heating and extracting gas from the samples, (2) an ultrahigh-vacuum purification line with SAES getters and a cold trap and (3) a Micromass 5400 noble gas mass spectrometer with a high sensitivity and an ultralow background. The mass spectrometer has a pulse counting system with an electron multiplier, which works effectively for the analysis of very small amounts of gas. Fish Canyon Tuff sanidine and the K₂SO₄ and CaF₂ crystals were heated using a defocused continuous CO₂ laser beam with a similar diameter to the grain size for 1 min. The samples of unknown age were ablated by a UV pulse laser at the following conditions: 50 µm beam size, 2 min pulse duration and 10 Hz repetition rate. The extracted gas was exposed to SAS getters and a cold trap, in which the metal fingertube was cooled to the freezing temperature of ethanol for 10 min to purify the sample gas to pure Ar gas. Finally, the purified Ar gas was introduced into the Micromass 5400 noble gas mass spectrometer to determine the Ar isotopic ratios. The Ar isotopic ratios of the sample gas were finally obtained after corrections of blank, mass discrimination by the analytical results of atmospheric argon, interference of the Ar isotopes derived from Ca and K by the irradiation, and the decay of the radiogenic Ar isotopes (³⁷Ar and ³⁹Ar) produced by the irradiation. The calculation of the ages and errors was performed according to Uto et al. (1997). The data are presented in Table 4.

RESULTS Petrographic and mineral chemical characteristics

A conspicuous feature of most MDMC rocks is the preservation of primary fabrics even at microscopic scale as a result of a general lack of penetrative internal deformation. In most metabasite samples a former subophitic texture of intergrown clinopyroxene and plagioclase crystals or a porphyritic texture with clinopyroxene phenocrysts (0.5-3 mm) in a feldspar-rich groundmass is variably preserved, although generally partly to completely pseudomorphed (Fig. 2). Amygdales with a mono- or bimineralic fill of quartz, chlorite, calcite and/or epidote (0.5-4.0 mm diameter; Fig. 2d) represent an additional common primary feature in the metabasites.

Clinopyroxene is augite with a widely variable composition (diopside₃₆₋₅₈, hedenbergite₇₋₁₅, enstatite₁₈₋₄₉, acmite₀₋₇, Tschermak component₀₋₁) including traces of Ti (0·004-0·019 a.p.f.u.) and Mn (0·003-0·011 a.p.f.u.). According to Sepúlveda *et al.* (2008) its composition is typical for non-alkaline basalts. Relict plagioclase compositions range between 48 and 79 and 19 and 27 mol % anorthite. Some samples contain chromite crystals in the groundmass, which are typically reddish brown, anhedral to euhedral grains (0·02-0·4 mm), commonly with an alteration halo. Internal deformation in the metabasites is represented only by fissures, mostly with a monomineralic fill of pumpellyite, chlorite, epidote, white mica or calcite.

The metamorphic assemblages in the metabasite are (Table 1):

- (l) actinolite-pumpellyite-epidote-chlorite-white micaalbite-quartz-titanite ± calcite;
- (2) pumpellyite-epidote-chlorite-albite-quartz-titanite ± calcite ± white mica ± K feldspar;
- (3) garnet (grandite)-pumpellyite-epidote-chloritealbite-quartz-titanite ± white mica;
- (4) actinolite-garnet (grandite) epidote-chloritewhite mica-albite-quartz-titanite ± pumpellyite ± K-feldspar ± calcite.

The metabasites of the MDMC appear to lack stilpnomelane, although this mineral was observed in the metachert of the DU (Sepúlveda, 2004). Metamorphic minerals are heterogeneously distributed and can form small monomineralic clusters of 0.2-1 nm size of chlorite, pumpellyite, epidote, titanite-chlorite intergrowths, garnet, actinolite or white mica (Fig. 2). The crystal size within the clusters is generally between 10 and 30 µm, but may be up to 100 µm for chlorite or actinolite. Titanitechlorite intergrowths form pseudomorphs probably after primary ilmenite. Actinolite, chlorite and pumpellyite mainly replace clinopyroxene, whereas white mica and to a lesser degree also epidote form pseudomorphs after plagioclase (Fig. 2).

In the metapsammopelitic rocks of the DU and DYU the relic clastic fabric is preserved without or with only a very low degree of recrystallization of quartz in the matrix. The size of the newly grown quartz grains in the matrix is <0.02 mm. Whereas a cleavage is well developed in the metapelites, the metapsammites show only an incipient banding of phyllosilicate and quartz-rich domains of millimetre spacing. Metamorphic white mica and chlorite grew parallel to the incipient cleavage. Detrital phyllosilicates are mechanically rotated parallel to the cleavage and bent. Some quartz clasts in contact with white mica show incipient pressure solution effects causing a slight shape-preferred orientation. The metapsammopelitic rocks still exhibit relic clastic components, predominantly angular to subrounded clasts of quartz, albite, white mica, biotite and minor K-feldspar. Lithic clasts are mainly shale, siltstone, quartzite, mylonite, rare basalt and rhyolite. Heavy minerals are mainly zircon and tourmaline as well as minor titanite, garnet, apatite, pyrite and Fe-Ti oxides.

The composition of white mica in the metabasite samples varies considerably, but the range is similar between samples (Fig. 3; Table 2): Si 3.07-3.54 a.p.f.u. with phengite compositions (Si >3·2 a.p.f.u.) predominating, very low Ti (0.00–0.02 a.p.f.u.) and intermediate X_{Mg} [Mg/ $(Fe^{2+} + Mg); 0.30-0.64]$. Notably, a considerable margarite component may occur in some white mica grains within samples 04CH18c, 04CH17c, MD06-5B, MD06-11D and MD06-8 (Ca 0.02-0.14 a.p.f.u.), whereas most grains are devoid of Ca. Similarly, the Na content varies considerably between grains of a single sample and between the studied samples (Na 0.005-0.150 a.p.f.u.). The erratic and occasionally high Ca and Na contents are incompatible with the low metamorphic grade as a result of the known solvus relationships (e.g. Chatterjee & Froese, 1975; Höck, 1974). It is assumed that small domains of margarite and paragonite are intergrown with potassic white mica and that the occasionally high Ca and Na contents actually represent mixed analyses of such domains. In sample MD9804 two generations of phengite with significant compositional differences, particularly regarding the calculated Fe³⁺ contents, were detected (Fig. 3, Table 2): white mica I (Si 3.68-3.73 a.p.f.u., Fe³⁺ 0.97-1.11 a.p.f.u., X_{Mg} 0.74-0.81and white mica II (Si 3.45-3.59 a.p.f.u., Fe³⁺ 0.00-0.36a.p.f.u., X_{Mg} 0.55–0.78). White mica I appears to be almost glauconite in composition according to the definition of Bailey (1980). In all metabasite samples occasional high calculated Fe³⁺ contents occur (0.06-0.14 a.p.f.u.). Mixtures of chlorite and phengite can be excluded as an explanation, because the white mica was analysed in clusters devoid of chlorite.

White mica in the metapsammopelites always occurs in two generations: detrital mica is characterized by larger grain size (0.05-4 mm), lower Si content (3.03-3.38 a.p.f.u.), higher Ti content (0.005-0.075 a.p.f.u.), higher Na content



Fig. 2. Photomicrographs showing clustering phenomena. (a, b) Former subophitic texture of clinopyroxene (Cpx) and plagioclase replaced by an assemblage of clusters of chlorite (Cll) growing at the expense of clinopyroxene, of titanite-chlorite intergrowths (TtCl) replacing ilmenite and of white mica (Wm) replacing plagioclase. On the left-hand side, chlorite (Cl2) fills a fissure that opened twice (see arrow); widths of images are 175 mm (sample 04CH17); (a) crossed polars' (b) parallel polars. (c) White mica cluster (Wm) replacing a plagioclase phenocryst cut by a late chlorite-filled fissure (arrows); in the upper part of the image white mica replaces smaller randomly oriented former plagioclase with interstices filled by titanite-chlorite clusters (TtCl); width of image is 0.7 mm (sample MD26); crossed polars. (d) Epidote clusters (Ep) replacing former plagioclase in an assemblage with clusters of chlorite (Cl) and titanite-chlorite intergrowths (TtCl); an amygdule filled by quartz and chlorite occurs in the upper left corner; width of image is 0.7 mm (sample MD9); crossed polars.

(0.02-0.16 a.p.f.u.) and more variable X_{Mg} (0.34-0.66)compared with metamorphic white mica (0.01-0.05 mm), which is invariably phengite (Si 3·35-3·50 a.p.f.u.; Ti 0.001-0.010 a.p.f.u.; Na 0.00-0.02 a.p.f.u.; X_{Mg} 0.52-0.62). White mica compositions in all samples mostly plot close to the ideal line of the Tschermak's substitution except for sample MD 9804 and partly MD 06-8 with considerable Fe^{3+} substitution (Fig. 3a). Only a few samples contain some metamorphic white mica grains (particularly sample MD 9804) with a reduced interlayer occupancy between 0.8 and 0.9 a.p.f.u., whereas most of the studied white mica have identical interlayer occupancies to those formed during low-grade conditions (e.g. Willner, 2005). The observed minor reduction of interlayer occupancy may be due to some substitution of the pyrophyllite component towards illite as a result of the

 $KAl^{IV} \square_{-1}Si_{-1}$ and $KR^{2+}Al^{VI} \square_{-1} \square_{-1}$ substitutions (R = Mg, Fe). According to an IMA recommendation the term illite should only be used for interlayer-cationdeficient micas with K + Na < 0.85 a.p.f.u. (Rieder *et al.*, 1998) and illite usually has an interlayer occupancy of c. 0.75 (Srodon & Eberl, 1984). Thus, at most, a small amount of illite is actually present in our samples. This concurs with similar observations made by the systematic study of Abad et al. (2006) that true illite compositions are rather rare with respect to muscovite-phengite compositions at very low grade and low-grade conditions. Similarly, muscovite and phengite has been reported from pumpellyite-actinolite-facies schists in the Swiss Alps and in New Zealand (e.g. Coombs et al., 1976, 1977). Interestingly, there is a systematic major element correlation in white micas: generally, a systematic variation of



Fig. 3. Si vs Al and Si vs X_{Mg} variations of white mica in the metabasite and metapsammopelite samples of the MDMC.

increasing X_{Mg} , a temperature-dependent parameter, with increasing Si content, a pressure-dependent parameter, can be observed (Fig. 3b).

Chlorite is ubiquitous in all samples. Chlorite generally shows a wide range of Si contents compared with a restricted $X_{\rm Mg}$ range within single samples (Table 2; Fig. 4). Conversely, $X_{\rm Mg}$ varies widely between samples (0·3–0·85) because of the variation in whole-rock composition, but also the range of Si contents within the samples varies considerably (5·4–6·8 a.p.f.u.). Mn is the only trace element with significant contents (0·02–0·06 a.p.f.u.; rarely up to 0·08–0·14 a.p.f.u.). No distinct chlorite generations as a result of compositional differences were detectable.

Garnet occurs as clusters of crystals (10–20 μ m size) in the metabasite samples MD98-03, MD98-04 and MD06-5B and is invariably grandite in composition (andradite_{37–46}, grossular_{50–6b} spessartine_{0.2-1.b}, pyrope_{0.1-1.7}, almandine_{0.0-2.4}, uvarovite_{0.0-2.0}). Rare elevated Cr

contents of 0.1-0.5 a.p.f.u. were locally detected in some grains in samples MD98-03 and MD98-04.

Epidote contains 67–98 mol % (mostly above 80 mol %) pistacite component (Table 2). The distribution of Fe within the grains is rather patchy. A different population of epidote was detected in three samples with considerably lower pistacite contents of 41–58 mol % (04CH18, MD26, MD05-18) or 25–27 mol % (MD26). The only notable minor element is Mn (0.005–0.018 a.p.f.u., occasionally up to 0.05 a.p.f.u.).

Amphibole is actinolite (Si 7·83–8·00 a.p.f.u.) with some calculated Fe³⁺ (0·03–0·59 a.p.f.u.), some Na^B contents (0·03–0·20 a.p.f.u.) and a high $X_{\rm Mg}$ (0·60–0·82). $X_{\rm Fe}^{2+}$ [Fe²⁺/(Fe²⁺ + Fe³⁺); 0·38–0·96] varies considerably, possibly as a result of variable oxidation fugacities.

Pumpellyite shows a positive correlation between $X_{\rm Fe}^{3+}$ [Fe³⁺/(Fe³⁺ + Al); 0·38–0·92] and $X_{\rm Mg}$ (0·62–0·94) as well as some trace elements; for example,



Fig. 4. Si vs X_{Mg} variation of chlorite in metabasite and metapsammopelite samples of the MDMC.

Ti (0·001–0·147 a.p.f.u.), Mn (0·000–0·025 a.p.f.u.) and Na (0·003–0·023 a.p.f.u.). Metamorphic feldspar is pure albite and/or K-feldspar. The latter mineral was observed in the metabasite samples MD98-04, MD05-18 and MD06-3B (Table 2).

General phase relations and metamorphic conditions

The prevalence of very low grade metamorphism in the MDMC is evident from the following observations. The general lack of quartz recrystallization in the matrix of the metagreywackes and preservation of datable radiolarians in the cherts (Ling *et al.*, 1985) associated with the DU metabasites suggest that maximum temperatures would not have significantly exceeded 300°C. Quartz fabrics in the metagreywackes resemble those of type C of Brix *et al.* (2002) that are shown to have prevailed at a temperature of 300–320°C. In addition, a temperature of about 280°C, at which fission tracks in zircon anneal at mean cooling rates (Rahn *et al.*, 2004), must have been reached or overstepped, because all detrital zircon in the two metagreywacke samples studied has been entirely reset (Thomson & Hervé, 2002).

The Kübler Index (KI; Kübler, 1968) is a common semiquantitative temperature indicator at very low grade to low-grade metamorphism that integrates over the strongly variable compositions of potassic white mica present in the rock. For the determination of the KI, four metapelite samples from a transitional contact zone between the DU and the DYU were analyzed. Samples MD04-IA and MD04-IB were taken from the DYU and samples MD04-8A and MD04-8AB represent red siliceous argillite from the DU intercalated within the chert. All samples were composed of white mica, chlorite, quartz and hematite. KI values vary as follows: 0.28 $\Delta^{\circ}2\theta$ for MD04-8AB and MD048A; 0.30 $\Delta^{\circ}2\theta$ for MD04-1A; 0.32 $\Delta^{\circ}2\theta$ for MD04-1B. These values correspond to anchizonal conditions representing temperatures between 200° and 300°C. No break of metamorphic conditions appears to exist between the major units of the MDMC.

An obvious lack of very low grade minerals such as laumontite and prehnite precludes metamorphism at LP conditions, including ocean-floor metamorphism. This agrees with the ubiquitous occurrence of metamorphic indicators of elevated pressure such as phengite. On the other hand, typical HP phases, such as lawsonite and Na-amphibole, are absent. The prevalent assemblages in the DU metabasites define conditions of the pumpellyite-actinolite facies at intermediate pressures. Figure 5 indicates the approximate limits of the actinolite-pumpellyite facies for the MDMC. The multivariant boundary reactions were calculated with averaged activities of end members of solid solutions in the system CMASH as realized in the rocks of the DU (for the method see below). The extent of the stability field of the actinolite-pumpellyite facies is largely defined by the presence of pumpellyite + chlorite. At the transition to the lawsonite-blueschist facies a subfacies field exists where both minerals coexist with glaucophane. It is notable that the pumpellyite-actinolite facies occupies an intermediate pressure field, corresponding to a geothermal gradient of $\sim 11-25^{\circ}$ C/km (calculated using 2.8 g/cm³ as the mean crustal density). This field also extends into the



Fig. 5. Petrogenetic grid for the pumpellyite–actinolite facies with limiting multivariant reactions calculated with mean activities of the following end-members in the system CNMASH as realized in the studied rocks (in parentheses): lw, lawsonite (1 0); gl, glaucophane (0·4); cl, chlinochlor (0·1); pu, Mg-pumpellyite (0·7); cz, clinozoisite (0·2); tr, tremolite (0·7); qz, quartz (1 0); ab, albite (1 0); v, H₂O fluid (1 0); pr, prehnite (1 0). Shaded area indicates the field of metamorphic gradients between 11 and 25° C/km.

field of HP greenschist facies (Fig. 5). It deviates strongly from the metamorphic geotherm of $8-10^{\circ}$ C/km typically deduced from HP–LT rocks that were overprinted directly above a subducting slab (e.g. Agard *et al.*, 2009) and presumably represents a hotter region of the subduction system.

Phase relations observed in *PT* pseudosections

For an advanced assessment of phase relations, geothermobarometric constraints and equilibrium conditions at very low to low grade we calculated PT pseudosections in the system K₂O-Na₂O-CaO-FeO-O₂-MgO-Al₂O₃-TiO₂-SiO₂-H₂O-CO₂ at 200-400°C and 1-9 kbar with the PERPLEX software package (Connolly, 1990, 2005; version of August 2006 downloaded from www.perplex .ethz.ch). The thermodynamic dataset of Holland & Powell (1998, updated 2002) for minerals and aqueous fluid was used. This dataset was recently enlarged using end-member data for Fe²⁺- and Fe³⁺-pumpellvite, Fe²⁺and Mg-stilpnomelane, actinolite and magnesioriebeckite (Massonne & Willner, 2008). Calculations were performed using the following solid-solution models: for white mica, epidote, chlorite and biotite by Holland & Powell (2003) and Powell & Holland (1999), grandite by Engi & Wersin (1987) and amphibole, sodic clinopyroxene, pumpellyite and stilpnomelane by Massonne & Willner (2008). The selected amphibole model provides a better adaptation to very low grade and low-grade conditions, whereas the selected clinopyroxene model is the Holland & Powell (1996) model supplemented by the aegirine component, which is often enhanced at very low grade conditions. The solid-solution models of white mica, epidote, chlorite, biotite and grandite were selected from the distributed version of the PERPLE-X solution model file. The solid-solution models of amphibole, sodic clinopyroxene, pumpellyite and stilpnomelane are added to this file as described by Massonne & Willner (2008). Albite, K-feldspar, quartz, titanite, H_2O and paragonite were considered as pure phases.

We selected five metabasite samples from the MDMC (MD5, MD26, MD98-04, 04CH18 and MD06-3) covering the entire range of observed assemblages (Table 1), and an additional metabasite sample (SLL853) from the very low grade Eastern Belt of the Chonos Archipelago for comparison. This sample contains a stilpnomelane-bearing assemblage that was not observed in the MDMC (Tables 1 and 3). In some samples a considerable amount of magmatic clinopyroxene remains despite complete reaction of this phase to form metamorphic phases in other samples. This amount was subtracted from the original bulk-rock analyses. Furthermore, for an optimal reproducibility of the

assemblages realized in the MDMC we used a slightly reduced oxygen content (uniformly 0.15 wt % O2, which is related to Fe³⁺ by the PERPLEX software) compared with the determined Fe₂O₃ contents of the rock. These Fe₂O₃ contents were higher than that of the metamorphic mineral assemblage because of the presence of hematite along grain boundaries formed by weathering. On the other hand, we kept the water content at the amount measured in the samples, because calculations with the PERPLEX software shows that at water excess conditions the entire rocks would have reacted to a higher quantity of hydrous minerals than observed. Although we included CO_2 as a component to calculate calcite, we did not consider it as a volatile component. Hence a pure H₂O fluid was used in the calculations for simplicity. However, corresponding calculations with a H₂O-CO₂ mixture have shown that the fluid is virtually entirely composed of H₂O at the selected PT conditions.

The *PT* pseudosections obtained (Figs 6–10; summary in Fig. 6) for the selected six metabasite compositions show a successful reproduction of the stability fields of the actual mineral assemblages within the pumpellyite–actinolite facies and also display the varying stability fields of critical very low grade phases that are consistent with phase relations as proposed and calculated by Katagas & Panagos (1979), Evans (1990), Frey *et al.* (1991) and Banno (1998) in the NC(F)MASH system (see also Massonne & Willner, 2008). Furthermore, selected calculated compositions of solid solutions (at approximate peak conditions of $5\cdot 6$ kbar, 300° C) concur well with analyzed compositions that are probably representative for peak metamorphic conditions (see Table 2).

Chlorite, amphibole and titanite are present at all calculated *PT* conditions. Pumpellyite in the presence of chlorite is stable within a very low grade field between 2 and 9 kbar and up to 300-350°C, whereas prehnite occurs below 3 kbar and 300–320°C. X_{Mg} $=X_{Mg}$ $(X_{Mg} + X_{Fetotal})$] in pumpelly ite rises with pressure and temperature with minimum values (0.40-0.46) below 3 kbar and 250°C (Figs 7 and 9). Lawsonite appears above 4-5 kbar and below 300-350°C. Laumontite occurs below 4-5 kbar and 300°C. Stilpnomelane can be stable in the entire very low grade field up to 300°C; biotite appears above 300-350°C. Epidote generally is a stable phase at very low grade conditions already between 200 and 250°C. Calculated Fe³⁺ contents are somewhat lower (0.6-0.64 a.p.f.u.) than those in the measured grains (0.8-0.9 a.p.f.u.). Grandite may be stable in the entire very low grade to low-grade field up to 350°C (Fig. 8) and has identical grossular/andradite compositions to those in the measured garnets (Table 2). K-feldspar and wairakite in metabasite occur below 3 kbar and 300-350°C and 2 kbar and 300-320°C, respectively. Amphibole is actinolite with Na contents up to 0.2 a.p.f.u. at 5 kbar and

 $X_{\rm Mg} = 0.6 - 0.8$ as observed in all studied MDMC metabasite samples. At low-grade conditions and at 6-8 kbar an intermediate Na-Ca-amphibole (0.2-0.5 Na p.f.u.; Figs 7–9) is stable. This mineral occurs within all regions of the Chilean basement that are interpreted to be accretionary complexes (e.g. Willner et al., 2001; Willner, 2005). Na-amphibole appears above 5-7 kbar at very low grade conditions and above 8 kbar at low-grade conditions. At very low grade conditions, two amphiboles may be present in the LP part of the lawsonite-blueschist facies (Figs 7 and 9), but one amphibole for Fe-rich bulk-rock compositions (Fig. 8). White mica is invariably phengite in the calculated PT field with Si contents increasing with pressure and decreasing with temperature. There appears to be a maximum of Si content of 3.4-3.5 a.p.f.u., particularly in the field of the pumpellvite-actinolite facies (Figs 7 and 9), coinciding with the analyzed phengite. Whereas X_{Mg} values of calculated and measured white mica grains deviate (e.g. 0.76 and 0.62, respectively, at 300°C and 5.6 kbar), those of chlorite are comparable (Table 2).

There is a remarkably good agreement of the metamorphic assemblages in the studied rocks with the six calculated assemblages at 290–310°C, 4–6 kbar (Fig. 10a). The appearance of stilpnomelane at these conditions was calculated and observed only for sample SLL853 from the Eastern Belt of the Chonos Archipelago. On the other hand, according to the pseudosections the former presence of stilpnomelane during the prograde PT path can be predicted for samples 04CH18, MD06-3 and MD5. Stilpnomelane disappeared at maximum PT conditions outside its stability field or never nucleated as a result of overstepping of reactions. Sample MD98-04 contains some epidote, which, however, appears at the high-temperature boundary of the field marked in Fig. 10a.

The conditions of the observed mineral assemblages appear to be realized at the high-temperature end of the pumpellyite-actinolite facies. Four samples show the stable assemblage actinolite-pumpellyite. Three *PT* fields concur with the approximate outline of the pumpellyiteactinolite facies as shown in Fig. 5. It should be noted that for two metabasite samples no realistic assemblages could be calculated. The whole-rock compositions are ultrabasic (MD066 and MD05-11D; Table 3) and the number of phases in the rocks is restricted (Table 1). This shows that considerable metasomatism, presumably caused by enhanced fluid flow, affected these two rocks at some stage, causing the low number of phases.

Geothermobarometry using multivariant equilibria

We also calculated PT conditions for the peak of metamorphism and different prograde equilibration stages using the entire range of variation of analyzed mineral compositions. We calculated multivariant reactions using the Ge0-Calc software of Brown *et al.* (1989) and derivations



Fig. 6. PT fields of minerals extracted from calculated pseudosections for the whole-rock compositions of the metabasite samples (see Table 3).



Fig. 7. Pseudosection calculated for the whole-rock composition of metabasite sample MD26 (see Table 3) with isopleths of Si a.p.f.u. in white mica, Na a.p.f.u. in amphibole and X_{Mg} in pumpellyite. Shading indicates degree of variance: white, divariant; light grey, trivariant; dark grey, quadrivariant.

(TWQ) with the thermodynamic dataset of Berman (1988) augmented by compatible thermodynamic data for the end-members glaucophane and Mg-pumpellyite by Evans (1990),clinochlore, Mg-Al-celadonite and Fe-Alceladonite by Massonne (1995a) and daphnite and muscovite by Massonne & Szpurka (1997). The activity formulations used for non-ideal solid solutions of garnet were those of Berman (1990), for chlorite and amphibole those of Massonne (1995a, 1995b), for white mica those of Massonne (1995a, 1997) and pumpellyite those of Evans (1990), whereas an ideal solution model was chosen for epidote $(a_{\text{clinozoisite}} = 1 - X_{\text{pistacite}})$. We preferred these data to those of Holland & Powell (1998) used for the calculation of pseudosections (see previous section) in order to obtain independent information on the maximum PT conditions

recorded. We have widely and successfully applied this approach to other low- and medium-grade rocks of the Chilean accretionary systems (e.g. Willner *et al.*, 2000, 2001, 2004; Willner, 2005). Hence, a better basis for comparison between the various Chilean accretionary complexes is given.

Because the above-described phase relations demonstrate adaptation to the conditions of the upper pumpellyite-actinolite facies without homogenization of mineral compositions, it is likely that transient prograde equilibria are locally preserved. Although it is difficult to find coexisting phases in mutual contact because of clustering of the phases, we tried to calculate local equilibria considering the wide compositional range of the relevant phases. Calculation results are shown in Fig. 11. For three samples



Fig. 8. Pseudosection calculated for the whole-rock composition of metabasite sample MD9804 (see Table 3) with isopleths of Si a.p.f.u. in white mica and Na a.p.f.u. in amphibole. Shading as in Fig. 7, and black, quintvariant.

 $(04\mathrm{CH18},\ \mathrm{MD26}$ and $04\mathrm{CH15})$ we applied the water-independent thermometer reaction

$$daphnite_{Ch}+5 Mg-Al-celadonite_{Wm}$$
(E1)
= 5 Fe-Al-celadonite_{Wm}+clinochlore_{Ch}.

This indicated a temperature range of $200-330^{\circ}$ C during metamorphic mineral growth. Similarly, application of the water-dependent thermometer reactions

$$25 \text{ Mg}-\text{Al-celadonite}_{\text{Wm}}+13 \text{ clinochlore}_{\text{Ch}}$$

+12 grossular_{Gr}+44 quartz = 18 tremolite_{Am} (E2)
+25 muscovite_{wm}+34 water

and

to samples MD05-06B and MD5, respectively, gave the same range, supporting our assumption that the fluid consists predominantly of H_2O .

A water-dependent barometer reaction

$$5 \text{ Mg-Al-celadonite}_{wm}$$
+muscovite_{wm}
= 2 quartz + 6 K-feldspar + clinochlore_{cl}+2 water
(E4)

was applied only to two K-feldspar-bearing samples (metapsammite MD06-8 and metabasite MD9804). In these samples calcite is absent and hence the water activity can be assumed to be unity. Although the pressure ranges for the two samples do not overlap, it is likely that the full range of compositions was not observed. Hence, a pressure range of 3–5 kbar at 200°C and 4–6 kbar at 300°C appears likely for the growth of minerals of the MDMC rocks also according to the *PT* calculation of mineral equilibria.

In sample MD9804 the *PT* intersection of 24 multivariant equilibria was calculated in the KCMASH system including K-feldspar and quartz and mineral end-members muscovite, Mg–Al-celadonite, Mg-pumpellyite, clinochlore, clinozoisite and grossular. Eight of these 24 equilibria are water-independent. The corresponding



Fig. 9. Pseudosection calculated for the whole-rock composition of metabasite sample 04CH18 (see Table 3) with isopleths of Si a.p.f.u. in white mica, Na a.p.f.u. in amphibole and X_{Mg} in pumpellyite. Shading as in Fig. 7, and black, quintvariant.

intersections calculated for three different local mineral assemblages vary between 230°C, 4.5 kbar and 240°C, 3.5 kbar.

For metabasite samples 04CH18 and MD26 the intersection of four multivariant reactions was calculated in the system KCFMASH including the mineral end-members muscovite, Mg–Al-celadonite, Fe–Al-celadonite, Mgpumpellyite, clinochlore, daphnite, clinozoisite and quartz. Only one of the four equilibria is waterindependent. The resulting PT intersections for each of the samples fall in the range 245–330°C, 3·9–5·8 kbar.

Summarizing the results of different but logical combinations of mineral equilibria to reconstruct transient local PT domains based on thermodynamic calculations, it can be shown that the observed variation in the chemical composition of the minerals reflects a range of temperatures that by far exceeds the narrow range of 290–310°C estimated for the peak metamorphic assemblage. Temperatures calculated for the local *PT* domains are up to 100°C lower at a similar pressure range. Some local PT domains, which are firmly constrained by the intersection of 24 multivariant equilibria, show temperatures that are 60° C lower than the derived peak T conditions. Considering an estimated error of $\leq \pm 30^{\circ}$ C for the geothermometers at relatively low temperatures, a common assumption (e.g. Holland & Powell, 1998), this temperature difference would be significant within error Hence, we interpret the local PT domains as prograde relics indicating that the late prograde PT path evolved from 4 ± 1 kbar, 200–220°C to 5 ± 1 kbar, 290–330°C and, thus, in the medium-pressure part of the pumpellyite-actinolite facies related to metamorphic geotherms between $13^{\circ}C/km$ (at the beginning) and $25^{\circ}C/km$. Maximum PT conditions are broadly identical to those derived from the



Fig. 10. (a) Calculated PT fields of the peak metamorphic assemblages observed in six selected metabasite samples. (b) PT fields of actinolite-pumpellyite for four selected metabasite samples.



Fig. 11. PT diagram showing the maximum PT spread of calculated reactions and equilibria. The approximate prograde PT path is shown (grey arrow).

calculation of the pseudosections. This result is, however, based on the assumption that all rocks in the study area evolved along similar PT paths, at least within the given PT range.

Ar/Ar geochronology

We analyzed the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ systematics of white mica in three metabasite samples (MD0511D, 04CH17c, 04CH18)

and one metapelite sample (04CH15) using the *in situ* UV laser ablation technique to obtain the age of the very low grade metamorphism. We selected this method because peak metamorphic temperatures in the MDMC are considerably below the commonly accepted value (\sim 350–420°C) of the white mica Ar closure temperature (McDougall & Harrison, 1999, and references therein) and, thus, the ages reflect white mica growth ages rather

than cooling ages. The UV laser ablation technique of Kelley *et al.* (1994) allows detection of age heterogeneities at thin-section scale. Although the beam size of 50 μ m exceeded the size of single crystals, clusters of only a few adjacent white mica crystals were analyzed. The white mica clusters in the metabasite are monomineralic, whereas the white mica in the metapelite is always intergrown with some chlorite. The presence of detrital mica in the metapelite is unlikely, because the selected slate 04CH15 represents a pelagic clay deposited on top of oceanic crust before metamorphism. The results are presented in Fig. 12 and Table 4. An earlier attempt to date titanite-chlorite clusters by U/Pb laser ablation failed because of the low U concentrations.

Three samples show a distribution of single-spot ages at thin-section scale with identical ages within the limits of the 1σ errors: a weighted mean age of 200.8 ± 2.4 Ma results for metabasite MD0511D, $233 \cdot 2 \pm 1.8$ Ma for metapelite 04CH15 and 152.0 ± 2.2 Ma for metabasite 04CH17c. The rather homogeneous spot ages in metapelite 04CH15 again demonstrate that no detrital white mica is present in the sample. On the other hand, metabasite 04CH18c shows a rather wide scatter of ages at thin-section scale ranging from 127.5 ± 32.4 to 206.9 ± 16.0 Ma, including substantial errors for the single-spot ages. Analyses of the metabasite samples generally show relatively high ${}^{37}\text{Ar}/{}^{39}\text{Ar}$ and ${}^{37}\text{Ar}_{\text{Ca}}/{}^{39}\text{Ar}_{\text{K}}$ values. We suggest that this is due to some contamination of the measured spots with titanite. Because titanite belongs to the same metamorphic assemblage as the dated white mica, no mixture of ages should be expected.

The weighted mean age of 200.8 ± 2.4 Ma for the metabasite MD0511D is identical to the normal and inverse isochron ages (196.4 ± 8.0 Ma and 199.3 ± 7.5 Ma respectively; Fig. 12) and its initial 40 Ar/ 36 Ar ratio of 302 ± 28 in the inverse isochron plot is close to that of atmospheric Ar (295.5). The inverse isochron plot reveals a simple mixture of radiogenic and 21–41% atmospheric Ar. Also, the weighted mean age of 233.2 ± 1.8 Ma for the metapelite 04CH15 is identical to the normal and inverse isochron ages (239.5 ± 8.6 Ma and 243.0 ± 8.3 Ma respectively) within the 1 σ error.

Both samples with considerably younger ages (04CH17c and 04CH18c) also show rather high contents of atmospheric Ar (52–93%) and their initial 40 Ar/ 36 Ar ratios of 291 ±3 and 305 ±3 are close to that of atmospheric Ar. In sample 04CH17c the weighted mean age of 152·0±2·2 Ma is nearly identical to the normal and inverse isochron ages (both 156·8±3·7). In sample 04CH18 the weighted mean age is calculated as 151 6±4·4 Ma, although single age values vary significantly from 128 to 207 Ma. Isochron ages of 128·6±7·8 Ma (normal isochron) and 128·5±7·6 Ma (inverse isochron) were obtained with an initial 40 Ar/ 36 Ar ratio of 305±3 for both isochrons. This

means that the Ar/Ar ages are variable or dispersed among spots against the initial atmospheric ⁴⁰Ar/³⁶Ar ratio of 295.5, or the Ar/Ar ages are identical or homogeneous around 129 Ma against the higher initial ⁴⁰Ar/³⁶Ar ratio of 305. Although the possibility of excess Ar cannot be excluded, we prefer the former interpretation, because the strong scatter of ages in sample 04CH18c appears to be due to a variable age resetting, with age values between those similar to samples MD0511 and 04CH15 and young ages as in sample 04CH17c that can be interpreted as a consequence of complete resetting. The weighted mean ages in samples 04CH17c and 04CH18c are identical, in accordance with their neighbouring outcrops, and can best be interpreted to date an age resetting event. During the retrograde PT path atmospheric Ar may have been introduced, presumably by meteoric fluids, which caused the resetting of the ages when a relatively shallow crustal level was reached. Because of a lack of internal deformation in the metabasite samples, any effect of deformation on age resetting can be excluded. Consequently, only the two older ages obtained from samples MD0511 $(200.8 \pm 2.4 \text{ Ma})$ and 04 CH15 $(233.2 \pm 1.8 \text{ Ma})$ can be related to the very low grade metamorphic event.

DISCUSSION Kinetically controlled metamorphic reactions

At present, much petrological work is focused on understanding the kinetic controls on mineral formation under variable metamorphic conditions as a result of dynamic disequilibrium processes (e.g. Carlson, 2002; Müller et al., 2009). Apparent disequilibria are ubiquitous phenomena at all metamorphic grades, but particularly during very low grade metamorphism of metabasic rocks. Considering a prograde PT path for basic rocks (which contain a significant proportion of unaltered magmatic minerals) hydrous fluid influx is required to enhance the progress of reactions, producing dominant hydrous phases such as amphibole, chlorite, white mica, pumpellyite or stilpnomelane. This is essentially due to fluid flux from adjacent dehydrating metapsammopelites. However, reactions proceeding locally within the metabasite during prograde metamorphism can also release hydrous fluids as a result of dehydration. A number of non-equilibrium effects are associated with the hydration and dehydration reactions. The incomplete, heterogeneous consumption of protolith phases such as clinopyroxene or plagioclase (Fig. 2) within and between samples could point to restricted availability of water. It was because of this assumption that the wholerock compositions for the calculation of pseudosections were corrected for the protolith phases and the amount of water was limited. The very small grain size of the reaction products particularly in the clusters reflects high

Table 4: Results of isotopic analysis for ${}^{40}Ar{}^{\beta9}Ar$ dating

Age (Ma)	±1σ	⁴⁰ Ar*/ ³⁹ Ar _K	±1σ	⁴⁰ Ar/ ³⁹ Ar	±1σ	³⁸ Ar/ ³⁹ Ar	±1σ	³⁷ Ar/ ³⁹ Ar	±1σ	³⁶ Ar/ ³⁹ Ar	±1σ	% ⁴⁰ Ar _{atm}	$^{37}\mathrm{Ar}_{\mathrm{Ca}}/^{39}\mathrm{Ar}_{\mathrm{K}}$		
Sample MD0.	11D; J	= 0-001698, ть	etabasite												
197-46	4·35	68·120	1.561	97-407	0.729	0.042	0.007	0.1951	0.0043	0·1024	0.0050	30.40	0.82	normal isochron age:	196·4±8·0 Ma
204.41	7·18	70·654	2.608	119-741	1.202	0.037	0.007	0.3495	0.0113	0.1711	0.0086	41·31	1 -47	MSWD	0.94
199·32	6·72	68·798	2.435	95·738	0·783	0.032	0.007	0.3836	0.0069	0.0948	0.0080	28·54	1.62	initial ⁴⁰ Ar/ ³⁶ Ar ratio:	309 ± 29
194·16	6.94	66·920	2.510	84·716	1.081	0.034	600·0	0·2980	0.0115	0.0631	0.0079	21.42	1.26	inverse isochron age:	199·3 ± 7·5 Ma
207-53	4.65	71 ·797	1.678	90·528	0·810	0.039	0.004	0.0626	0·0032	0.0657	0.0052	21·03	0·26	MSWD	1·00
199·16	7·23	68·739	2.621	98·504	1.450	0.041	0.006	0·2098	0-0070	0·1041	0·0081	30·55	0·89	initial ⁴⁰ Ar/ ³⁶ Ar ratio:	302 ± 28
			:											weighted mean	200·8±2·4 Ma
Sample 04CF	115; J=	<i>0-001707, met</i> s	apelite												
230-96	3·09	80·010	1·093	115-535	0.757	0·048	0.004	0.0677	0·0042	0·1237	0·0033	31·04	0·30	normal isochron age:	239·5±8·6 Ma
235-58	4.96	81·719	1·808	111·175	0·876	0·037	0·004	0·0884	0·0069	0·1029	0.0057	26·81	0.39	MSWD	1·48
246·13	5.29	85·631	1·938	111·119	0.950	0.039	0.003	0.0290	0.0047	0.0891	0.0061	23·25	0.13	initial ⁴⁰ Ar/ ³⁶ Ar ratio:	272 ± 27
229-47	4·32	79-461	1.562	105·112	0.696	0·029	0.004	0.0376	0.0040	0.0896	0.0050	24.71	0.16	inverse isochron age:	243·0±8·3 Ma
223·96	5.79	77 ·432	2.105	125·297	1.151	0.050	0.006	0·0342	0.0043	0·1661	0·0068	38.45	0.15	MSWD	1·58
236·87	4·86	82·194	1.769	119-547	1.400	0.039	0.006	0.0353	0.0051	0·1299	0·0052	31.53	0.15	initial ⁴⁰ Ar/ ³⁶ Ar ratio:	264 ± 27
														weighted mean	233·2 ± 1·8 Ma
Sample 04Ch	117; J=	0-001707, meti	abasite												
143·47	5·84	48·491	2·045	279-976	2·575	0·172	0.008	0.5578	0-0122	0.7996	0·008	82·79	2.39	normal isochron age:	156 \cdot 8 \pm 3 \cdot 7 Ma
155·05	5.94	52·573	2·092	141·501	1.117	0·082	0.007	0·4106	0·0082	0·3082	0.0070	63·06	1.77	MSWD	0.56
143·98	14·61	48·670	5·133	373·883	5·164	0·222	0.015	0.6585	0.0206	1·1228	0·0221	87·07	2·84	initial ⁴⁰ Ar/ ³⁶ Ar ratio:	291 ± 3
155·00	11·68	52.556	4·127	285·332	2·282	0·178	0.00	0.5030	0.0133	0·8040	0·0149	81·69	2.17	inverse isochron age:	156·8±3·7 Ma
143·85	11·08	48·625	3·892	204·786	2.372	0·126	0.011	0·2639	0.0104	0.5394	0·0132	76·38	1.14	MSWD	0-57
153·96	2.79	52·191	0.965	108·232	0.606	0.049	0.005	0·2341	0.0046	0·1944	0·0032	52·02	1.01	initial ⁴⁰ Ar/ ³⁶ Ar ratio:	291±3
														weighted mean	152·0±2·2 Ma
Sample 04CH.	418c; J=	= 0-001697, me.	tabasite												
196·16	24-48	67·687	8-911	438·379	9·719	0·296	0.018	0.9554	0·0298	1·2809	0.0407	84·69	4·27	normal isochron age:	126.6 ± 7.8 Ma
171-76	13·21	58·861	4.740	528·686	10·748	0·344	0.020	2·0982	0.0507	1.6255	0.0363	89·01	9.43	MSWD	1·42
127·50	32·37	43·153	11·347	402·531	10·744	0·344	0·026	4·7883	0·1380	1·2513	0.0500	89·55	21·80	initial ⁴⁰ Ar/ ³⁶ Ar ratio:	305 ± 3
142·44	6·88	48·412	2.425	166·784	2.676	0·114	0.007	0.9394	0.0212	0.4110	0·0100	71·21	4·21	inverse isochron age:	128·5 ± 7·6 Ma
136·76	7·94	46·407	2.792	215·763	3·721	0·131	0.015	0·2919	0·0128	0.5849	0.0133	78·60	1·31	MSWD	2·8
167-41	18·94	57·299	6·785	762·850	18·989	0·472	0·028	2·6483	0.0765	2.4391	0.0640	92·61	11·97	initial ⁴⁰ Ar/ ³⁶ Ar ratio:	305 ± 3
206·92	16·00	71·616	5.856	544·518	11·612	0·348	0·022	2·6402	0.0607	1.6383	0.0395	87·05	11.95	weighted mean	151·6±4·4 Ma

FRONTAL ACCRETIONARY PRISM EVOLUTION



Fig. 12. Probability curves and weighted average ages for Ar/Ar spot ages of four samples. Dots indicate single *in situ* spot ages (with 1σ error bars).

nucleation and growth rates, with nucleation rates exceeding growth rates because of a high reaction affinity, which is a measure of the departure from equilibrium or the degree of overstepping (Roselle *et al.*, 1997).

Erratic compositional variations, such as margarite and paragonite domains in white mica, occasional elevated Cr contents in garnet or occasional elevated Mn contents in epidote, may be due to local variations in the whole-rock composition that were not homogenized during the metamorphic reactions. Intergranular diffusion rates are particularly low at very low temperature and those for elements such as Ca, Mn and trivalent elements such as Cr are considerably more sluggish than for common elements such as Fe and Mg (Carlson, 2002).

Variable Fe³⁺ contents in amphibole, white mica and pumpellyite are expressions of variable local buffering of fluids and/or diverse generation of external fluids. This may also explain different filling of fissures. For instance, Massonne & Willner (2008) noted that at 5 kbar, metapsammopelite and MORB mostly dehydrate at 230–250°C and 270–300°C, respectively. This means that at very low grade conditions the source and amount of the fluids may be variable and the amount restricted to specific *PT* conditions.

Mineral phases are not randomly distributed, but occur in nearly monomineralic clusters. The size of these clusters is generally controlled by the size and distribution of the protolith phases (Fig. 2). Clustering means that the distance between reaction partners varies strongly and hence influences intergranular diffusion and reaction progress.

The composition of the fine-grained metamorphic phases varies considerably, even within clusters. The X_{Mg} ratios of white mica, chlorite, amphibole and pumpellyite, as well as the Si contents of white mica and chlorite, show systematic variation within a restricted compositional range (Figs 3 and 4). This points to a temporary and local approach to equilibrium conditions.

It should be emphasized that the observed fine-grained fabric and the compositional variation strongly contrast with those of low-grade rocks in other Chilean accretionary systems metamorphosed at \sim 350–400°C (e.g. Willner *et al.*, 2000, 2001; Willner, 2005). Here recrystallization and compositional homogenization occurred throughout the rocks. Similarly, Brix *et al.* (2002) pointed out that above 320°C the grain size of the quartz fabric rapidly rises by an order of magnitude by complete recrystallization.

The described compositional variation and fabric effects may be explained by channelized and episodic infiltration of hydrous fluids that are heterogeneous in terms of composition including oxygen fugacity and amount, even at thin-section scale, as well as by kinetic control of mineral reactions. Of course, such processes appear to contradict and complicate the use of the applied geothermobarometric methods, challenging any attempt to define their precision. However, similar to mineral-zoning phenomena at higher metamorphic grade, the apparent nonequilibrium conditions provide a chance to decipher the PT conditions of prograde metamorphism. Hence, consideration of some locally preserved transient equilibria results in a reasonably consistent variation of conditions of mineral growth within a restricted PT range from about 4 ± 1 kbar, 200–220°C to 5 ± 1 kbar, 290–330°C. The strong scatter of mineral compositions must at least partly be due to dynamic equilibration along the prograde PT path leading to mineral growth over about 100°C within a narrow pressure range. This reflects near-isobaric prograde heating. There is little indication of retrograde mineral growth as is common under low-grade conditions in deeper (basally accreted) levels of other Chilean accretionary systems (e.g. Willner, 2005). The existence of potassic feldspar with a stability field at low pressure (Fig. 5) and some indication of late replacement by white mica as partly indicated by the Ar/Ar ages (see also below) may be taken as evidence that fluid flow and hence mineral growth did not entirely cease at peak metamorphic conditions.

The observed metamorphic assemblages can be reproduced within a rather limited PT range (290-310°C, 4-6 kbar) by calculation of PT pseudosections, although the modal amount of the produced phases varies significantly. The calculated compositions of minerals within this PT space reasonably coincide with those in nature. This demonstrates that adaptation of the metamorphic assemblage to the prevailing PTX conditions in fact took place on a thin-section scale, at least in the higher temperature part of the very low grade metamorphic range. This may be partly due to the fact that fluid infiltration was rapid and strongest around 300°C, in agreement with the findings of Massonne & Willner (2008) that in metapsammopelitic rocks of accretionary prism complexes a maximum amount of dehydration must have occurred at 230-250°C releasing hydrous fluids for reactions in the metabasic rocks. Müller et al. (2009) showed that a fluid infiltration controlled, carbonate thermometer reaction advanced rapidly to the recorded maximum temperatures, thus, preserving 'frozen in' lower temperature compositions. Stilpnomelane that should occur at the intermediate temperatures of the pumpellyite-actinolite facies according to the calculated pseudosections probably did not nucleate, as a result of overstepping of reactions or reduced availability of fluids at that stage. However, it grew at 300°C in the rocks of the Eastern Belt of the neighbouring Chonos Metamorphic Complex, where identical peak PT conditions to those in the MDMC were previously deduced by Willner et al. (2000). For the same reason the pseudosections can successfully be used as a petrogenetic grid

showing the growth of the actual assemblages in the metabasites of the MDMC within the pumpellyite–actinolite facies, bounded by the stability fields of lawsonite, laumontite, prehnite and biotite.

Significance of the prograde PT path

The proposed partial, nearly isobaric, prograde PT path points to a long-term adjustment to thermal conditions outside the subduction zone during subhorizontal particle paths at maximum depth (Fig. 13). Subhorizontal particle paths in frontal accretionary prisms at maximum depths are implied by the flow field concept of Ring et al. (1999) and are also observed in analog modelling (Kukowski et al., 2002; Glodny et al., 2005). They result from duplex stacking during build-up of the frontal accretionary prism. The subhorizontal particle flow paths cross the isotherms of the temperature field of the convergent margin towards higher temperatures, resulting in a finally preserved relatively high metamorphic gradient that strongly deviates from a geotherm realized along the top of the subducting slab. The peak conditions derived here approximate to an intermediate metamorphic geotherm of 17°C/ km. As subduction in the Phanerozoic has commonly occurred with plate velocities >3 cm/a, causing rather low geothermal gradients of $\leq 10^{\circ}$ C/km, rising geotherms at the deepest levels reached imply temporal residence and thermal re-equilibration over a certain period of time, before exhumation and cooling started (Fig. 13). The extraction of subhorizontal PT paths from frontally accreted parts of subduction systems produced by thermomechanical modelling proves the deduced relationship (Willner et al., 2008). However, it should be noted that the described effect is not the only possibility leading to elevated metamorphic geotherms. Such geotherms may also result, for example, from very slow subduction or subduction of hot young oceanic crust, according to numerical experiments by Peacock (1996). However, these alternative heating effects are special cases that would mainly affect the temperature field of the subduction channel, whereas the proposed thermal re-equilibration at depth after accretion appears to be a process characteristic of frontal accretionary prisms. It appears unlikely that geotherms as high as those observed in the studied metabasite will develop in the subduction channel.

Significance of the Ar/Ar ages

Compositional heterogeneity at a thin-section scale could also imply Ar/Ar age heterogeneity, because all derived Ar/Ar ages should be interpreted as ages of mineral formation owing to mineral growth considerably below the closure temperature of the K/Ar system. Age heterogeneities at thin-section scale, even in very low grade rocks, can be much better resolved with the *in situ* Ar/Ar UV laser ablation technique than by analyses of bulk concentrates. We obtained two ages related to very low grade



Fig. 13. Simplified schematic visualization of the possible thermal field around a growing frontal accretionary prism indicated by thrusts and folds. Grey area, subducting oceanic slab; dotted grey lines, isotherms; black arrows, active thrusts; grey arrows, inactive thrusts. Subhorizontal mass flow paths (black dashed arrows) result during the build-up of the prisms that cross the isotherms towards higher temperatures.

metamorphism in the DU by demonstrating homogeneous white mica age distributions at thin-section scale of 200.8 ± 2.4 Ma and 233.2 ± 1.8 Ma (Fig. 12). The measured single-spot ages of white mica in each sample did not vary within the 1σ error. Mineral growth was evidently timerestricted and this behaviour contrasts with results in lowgrade rocks of the metamorphic basement of the Coastal Cordillera in central Chile, where an age scatter results from continuing mineral growth along the retrograde PT paths (Willner et al., 2005). The homogeneous age distribution in sample 04CH15 $(233 \cdot 2 \pm 1 \cdot 8 \text{ Ma})$ is presumably caused by prograde growth of oriented white mica during deformation of the rock. This deformation represents the accretion process. The resultant age is compatible with the maximum depositional age of the DYU of about 270 Ma revealed by the youngest detrital zircon SHRIMP age (Hervé et al., 2003) and two fission-track zircon ages of $209 \pm 14/12$ Ma (Thomson & Hervé, 2002). The latter ages reflect a time of cooling after the peak of metamorphism, because the temperature of fission-track annealing in zircon of around 280°C was just overstepped. The age of 200.8 ± 2.4 Ma of the unoriented white mica clusters replacing plagioclase in sample MD0511 is younger than the FT zircon ages. This Ar/Ar white mica age may represent growth at peak PT conditions during a later stage of build-up of the accretionary prism, because sample MD0511 occurs about 4 km west of the samples used for FT dating and the older sample 04CH15. Alternatively, it may represent a retrograde stage of mineral growth.

Thomson & Hervé (2002) detected a similar peak metamorphic age in the Eastern Belt of the Chonos Metamorphic Complex (Fig. 1), bracketed by a young detrital zircon SHRIMP age of 207 ± 6 Ma and a fissiontrack zircon age of 210 ± 12 Ma. Here, very low grade metamorphic conditions identical to those in the MDMC

prevailed (Willner et al., 2000). Therefore in the two Patagonian accretionary systems (MDMC and CMC) metamorphism in the upper, frontally accreted, levels is about 100 Myr younger than in central Chile, where the equivalents (Eastern Series) were accreted before 300 Ma (Willner et al., 2005). This also appears to apply to the accretionary systems to the east of the Patagonian batholith, the East Andean Metamorphic Complex, where at least in its northern part maximum depositional ages of 311-353 Ma (Augustsson et al., 2006) and zircon fissiontrack ages of 253-267 Ma (Thomson & Hervé, 2002) point to similar ages of accretionary activity to those in central Chile. Hence the younger ages of metamorphism of the CMC and the MDMC point to a coherent Late Triassic-Early Jurassic event and thus the youngest fossil accretionary system exposed along the coast of Chilean Patagonia. On the other hand, the age of the structurally underlying and hence younger, basally accreted Western Belt of the CMC is as yet unknown. The MDMC is at least in tectonic contact with a rather small, basally accreted complex, the Diego de Almagro Metamorphic Complex (DAMC). The age of the peak of metamorphism in the DAMC is considered to be around 117 ± 28 Ma (K/ Ar; Willner et al., 2004). Volcanic rocks formed at 157 ± 2 Ma were overprinted within the DAMC (Hervé et al., 2003). The age relations between the MDMC and the DAMC confirm that in this region frontal accretion also occurred prior to basal accretion as has been recognized in central Chile (Richter et al., 2007).

The basement rocks were partly overprinted at 152.5 ± 2.2 Ma over a short distance (c. 2 km) from the Patagonian batholith (04CH17c and 04CH18c; Fig. 1). In sample 04CH18c relict ages as old as 207 Ma and a scatter of younger ages prove an incomplete resetting of ages originally similar to those of the peak of HP metamorphism. The overprinted metabasite samples also contain a little muscovite in addition to phengite, which might indicate, at least partly, new mineral growth during a partial LP overprint. This overprint, however, appears to be incompatible with heating by the closest pluton of the Patagonian batholith, which intruded later at 133 ± 1 Ma (Hervé et al., 2007a). Also, contact metamorphic effects are observed only at the immediate contact of the pluton and there is no indication that the maximum temperature of $\sim 300^{\circ}$ C was exceeded in sample 04CH18c. Additionally, deformation is not a factor, because internal deformation is absent within the analyzed samples. It is proposed that access of variable amounts of external hydrous fluids at some stage after the peak of metamorphism caused the local resetting of ages. McDowell & Elders (1980) reported 'illitization' of muscovite in the Salton Sea System at temperatures $\leq 280^{\circ}$ C, causing an apparent younging of ages. This process would imply partial or complete replacement of white mica. If the spacing of the replacement zones or lamellae is smaller than the beam size of the UV laser, a mixed age between the intrusion age of the nearby pluton and that of the replacement lamellae would be feasible. On the other hand, the obtained late Jurassic overprint age, if replacement of white mica is complete, could be related to the first bimodal intrusive activity of the South Patagonian batholith at 157–145 Ma (Hervé *et al.*, 2007*a*). This activity was due to an extensional event causing crustal thinning, an increase of the geothermal gradient and finally advection of hydrothermal fluids at shallow crustal levels.

CONCLUSIONS

In the Madre de Dios Metamorphic Complex mineral assemblages of the intermediate-pressure and hightemperature part of the actinolite-pumpellyite facies are formed. Different peak metamorphic assemblages observed in six metabasite samples suggest equilibration on a thin-section scale at 290-310°C and around 5 kbar. Furthermore, it has been shown that local equilibria are preserved despite strong compositional heterogeneity of the metamorphic phases, because of restricted availability of hydrous fluids, with presumably variable compositions and a lack of later compositional homogenization owing to the low temperatures attained. Calculated PT data indicate metamorphism along a nearly isobaric, prograde PT path, which in turn reflects a subhorizontal particle path in the frontal accretionary prism and a long-term thermal re-equilibration at maximum depths. This is in agreement with current concepts about the formation of frontal accretionary prisms. The prograde information preserved in the very low grade rocks strongly contrasts with that from the low-grade rocks of other Chilean accretionary systems, where recrystallization and compositional homogenization is complete and retrograde PT information is recorded.

The Ar/Ar spot ages do not vary at thin-section scale in three samples, but reflect ages of rapid growth of white mica at very different stages of the evolution of the accretionary prism. Only the age of $233 \cdot 2 \pm 1.8$ Ma can unambiguously be related to accretion, indicating that accretion in the MDMC started shortly before or around that time. Growth of white mica at $200 \cdot 8 \pm 2 \cdot 4$ Ma may be due to an advanced stage of accretion or a retrograde resetting effect. Much younger growth of white mica at $152 \cdot 0 \pm 2 \cdot 2$ Ma is clearly a later local resetting effect caused by access of external fluids, which were generated either during a postaccretionary extensional event or by a nearby igneous intrusion.

The Late Triassic age of accretion in the MDMC is identical to that of the upper part of the Chonos Metamorphic Complex in the north but in contrast to the Carboniferous frontal accretion in central Chile and to the east of the Patagonian batholith. This could be in line with migration of accretion mass flow processes with time from east to west as well as from north to south.

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SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal* of *Petrology* online.

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