A new activity model for Fe–Mg–Al biotites: II—Applications in the K_2O –FeO–MgO– Al_2O_3 – SiO_2 – H_2O (KFMASH) system

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Abstract

The new biotite activity model and standard-state thermodynamic properties of Ann, Phl, and Eas presented in part-I were used to make pseudosections of bulk compositions representing experimental Fe–Mg exchange equilibria and (model) pelitic bulk rock compositions in the system K_2O –FeO–MgO– Al_2O_3 – SiO_2 – H_2O (KFMASH), using mainly the software *Perple_X*. These pseudosection calculations (termed ‘*our calculation(s)*’ in the following) were compared to analogous ones performed with the solution model of biotite and thermodynamic data cited in White et al. (J Metamorph Geol 32:261–286, 2014, 10.1111/jmg.12071), termed ‘*W14 calculation*’. *Our calculations* with the experimental bulk composition used by Zhou (Ti–Mg–Fe biotites: formation, substitution, and thermodynamic properties at 650 to 900 °C and 1.1 Kb with fO_2 defined by the CH_4 –graphite buffer. PhD thesis, State University of New York, 1994) in his experimental study of the Fe–Mg exchange between biotite (Bt) and olivine (Ol) confirm that biotite had no or only minimal octahedral Al (Al^{VI}) in these experiments. The experimental data of Ferry and Spear (—FS78, Contrib Mineral Petrol 66:113–117, 1978, 10.1007/BF00372150) on the Fe–Mg distribution between biotite and garnet (Grt) are well reproduced by *our calculations*. The computed composition of biotite (X_{Fe}) in equilibrium with garnet of $Alm_{90}Py_{10}$ composition and the resulting $\ln K_D$ values as a function of temperature are in good agreement with the experimental brackets. An analogous *W14 calculation* on the same Fe-rich bulk composition predicts too high X_{Fe}^{Bt} in order of 0.1 mol fraction. The Al^{VI} contents of biotite of about 0.3–0.45 apfu, as measured by Gessman et al. (Am Mineral 82:1225–1240, 1997, 10.2138/am-1997-11-1218) in similar biotite–garnet exchange experiments performed with $Alm_{80}Py_{20}$ and $Alm_{70}Py_{30}$ garnets, are well reproduced by *our*, as well as by *W14 calculations*. The extent of Tschermak substitution in biotite in the FS78 experiments, which had Fe-richer bulk compositions, has not been measured. Comparing the FS78 biotites with the ones from Gessman et al. (Am Mineral 82:1225–1240, 1997, 10.2138/am-1997-11-1218), it is very likely that the biotites reported in FS78 contained Al^{VI} in the same order of ca. 0.3–0.4 apfu. A T – X_{Fe} (= molar FeO/(FeO + MgO)) pseudosection demonstrates the bulk composition dependence of $\ln K_D$ of the $Mg/Fe^{Grt/Bt}$ exchange reaction in high-variance fields. Further comparisons, demonstrating the application of the new biotite solution model in the KFMASH system, are presented in pseudosections constructed for an average model pelite, as well as for a natural high- T /low- P and a natural high- P metapelite. The pseudosections show that biotite according to *our* biotite model breaks down at lower temperatures and pressures than predicted from the *W14* biotite model in the KFMASH system. This means that KFMASH biotite can break down before the wet solidus is reached, which can explain the existence of dry high- T /low- P metapelites. At higher pressures, biotite according to *our calculations* breaks down at lower pressures than computed with the *W14* biotite model. Before biotite breaks down, however, its Al^{VI} content based on *our calculations* could potentially be used for pseudosection barometry, similarly as the Si-in-phengite barometer. These trends need to be confirmed by a future extension of our model which incorporates Ti, Fe^{3+} and a di–tri–octahedral substitution.

Keywords Biotite · Activity model · Solution model · Annite · Phlogopite · Standard enthalpy of formation · KFMASH · Pseudosection modeling

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Introduction

In part-I, a new KFMASH activity model was presented for biotite, an important rock-forming mineral. Mixing parameters and standard-state properties were derived through an integrated approach combining results from relaxation calorimetry, from powder XRD and line-broadening in powder absorption infrared (IR) spectra of well-characterized biotites with the thermodynamic analysis of existing phase-equilibrium data, complemented by density functional theory (DFT) calculations.

The aim of this part-II is to demonstrate the impact of this new biotite model on computed phase relations in the KFMASH system and comparing these phase relationships with those obtained with the biotite solution model of White et al. (2014).

Computational methods

As a general remark, we use in all applications the activity–composition (a – X) relations for biotite as outlined in part-I with mixing properties given in Table 8 and standard-state thermodynamic properties for annite (Ann), phlogopite (Phl), and eastonite (Eas) given in Table 9 of the companion paper. For alternative versions of our biotite model with symmetric W_{AnnPhl}^G and symmetric/asymmetric W_{AnnPhl}^G obtained from thermodynamic analysis of the olivine–biotite exchange equilibrium using a W_{FaFo}^G of 10 kJ/mol instead of 5 kJ/mol (one-site), we used the modified thermodynamic parameters as given in the discussion section of part-I (in the first paragraph entitled ‘standard enthalpy of formation values of biotite endmembers’). All other thermodynamic properties are those from the endmember database of Holland and Powell (2011), version ‘ds62’, and the a – X relationships of White et al. (2014) for solid solutions. These solid solutions were calibrated specifically for metapelite rocks. For certain pseudosections, we used, in addition to the solid solutions mentioned in White et al. (2014), the talc model of Holland and Powell (1998) and the olivine model of Holland and Powell (2011) with the W_{FaFo}^G corrected to 5 kJ/mol (one-site). We compare the phase diagram calculations using *our biotite model* to predictions made with the biotite model included in the a – X relationships of White et al. (2014, *W14*), keeping everything else the same.

Self-written programs in *Mathematica*® were used for computing the equilibrium Fe–Mg distribution between biotite and olivine (Fig. 1) and biotite–orthopyroxene (Opx) (Fig. 2). For this purpose, self-written routines were generated to calculate the thermodynamic functions describing the exchange. The a – X relations of olivine were based on a symmetric $W_{\text{FaFo}}^G = 5$ kJ/mol (one site, see discussion in

part-I), and those of orthopyroxene were calculated according to White et al. (2014) (Figs. 3, 4, 5).

Phase relations shown in Figs. 6, 7, 8, 10, 11, 13 and 14 and data given in Table 2 were computed with *Perple_X* suite of programs version 6.9.0. We used the program *vertex* for making pseudosections (Connolly 2005, 2009) using the bulk compositions, as given in Table 1. The equation of state for H_2O was that of Pitzer and Sterner (1995). In *our calculations*, the thermodynamic data file was *hp62ver.dat* with data for the biotite endmembers annite, phlogopite, and eastonite substituted by corresponding ones from Table 9 of part-I. This dataset in *Perple_X* format is given in Supplementary Table S1. In a *W14 calculation*, the original annite, phlogopite, and eastonite data from *hp62ver.dat* were used. The biotite activity model presented in part-I was coded for *Perple_X* and incorporated in *solution_model.dat* named Bio(D). It is also given in Supplementary Table S1.

Mineral–chemical quantities like Al^{VI} or mole fraction $X_{\text{Fe}} = \text{Fe}/(\text{Fe} + \text{Mg})$ in biotite and in other minerals were computed with the *Perple_X* program *werami* and appear as isopleths in the various pseudosections. The $\ln K_D$ for the garnet–biotite Fe–Mg exchange reaction (Figs. 3, 4, 5, 9) and contours of $\ln K_D$ (Fig. 8) were computed by self-written Mathematica functions processing data files containing X_{Fe} and X_{Mg} of biotite and garnet as a function of temperature and/or pressure/bulk composition, produced with *werami*.

Supplementary calculations were done with *Theriak* (de Capitani and Brown 1987; de Capitani and Petrakakis 2010) in case of the garnet–biotite Mg/Fe exchange reaction (Table 2) using the *Theriak* version 09. 03. 2019 and the database *tcds62c*. The new standard-state data, and our new biotite activity model in *Theriak* readable format, are given in Supplementary Table S2. Mineral abbreviations used in the text and figures are according to Whitney and Evans (2010).

Applications of the new biotite activity model in the KFMASH system

Experimental Fe–Mg exchange equilibria involving biotite

Notice that the experimental olivine–biotite equilibrium was used for the calibration of our model. In contrast, biotite–orthopyroxene, biotite–garnet, and biotite–garnet–cordierite equilibria were not and could, therefore, be used for validation purposes.

Biotite—olivine

The experimental data of Zhou (1994) on the Fe–Mg exchange between biotite and olivine have been used in

Fig. 1 Roozeboom plot of the experimental data of Zhou (1994) on the Fe–Mg exchange between biotite and olivine ($P = 1.1$ kbar) in terms of $X_{\text{Fe}}^{\text{Ol}}$ vs. $X_{\text{Fe}}^{\text{Bt}}$ at $T = 800$ °C (a) and $T = 700$ °C (b). Starting compositions are shown as black dots, which are connected to the final compositions (red dots) with a line. Recalculated curve using the biotite activity model and thermodynamic data from *this study* (Tables 7, 8 of part-I) is shown in red, and for comparison in blue using the thermodynamic data and activity models cited in White et al. (2014)—W14

Fig. 2 Roozeboom plot of the experimental data of Fonarev and Konilov (1986) on the Fe–Mg exchange between biotite and orthopyroxene ($P=4.9$ kbar) in terms of $X_{\text{Fe}}^{\text{Opx}}$ vs. $X_{\text{Fe}}^{\text{Bt}}$ at $T=700$ °C. Starting compositions are shown as black dots, connected to the final compositions (red dots) with a line. The recalculated curve resulting from *this study* is shown in red and in blue from a *W14* calculation

part-I, combined with other experimental data to calibrate Fe–Mg biotite mixing properties and to derive enthalpy of formation values for annite, phlogopite, and eastonite. They are presented in Fig. 1a, b, together with recalculated *our-study* Roozeboom plots, made using the program Mathematica®, based on the reaction:

and compared to a *W14* calculation (details of the experimental setup, starting materials, and biotite composition were given in part-I). Although *our-study* and *W14* Roozeboom plots were calculated using considerably different biotite activity models and thermodynamic data for annite and phlogopite, the computed $X_{\text{Fe}}^{\text{Ol}}$ vs. $X_{\text{Fe}}^{\text{Bt}}$ curves are quite similar, satisfying the compositional brackets within error (Fig. 1a (at 800 °C), b (at 700 °C), the other isothermal Roozeboom plots are given in Supplementary Fig. S1). The only exception is at Fe-rich conditions, where *our calculation* predicts a somewhat lower $X_{\text{Fe}}^{\text{Bt}}$ in better agreement with the experimental record. This is, of course, not surprising, as Zhou's data have been used in part-I to calibrate Fe–Mg biotite mixing properties based on the assumption

that these experiments indeed represent equilibrium Fe–Mg distributions between olivine and biotite.

Zhou (1994) used biotite:olivine weight ratios of 1:1, 2:1, or 1:2 in his experiments; however, it is not clear from his tables which ratio was used in which run. We constructed an appropriate bulk composition for his experiments at 800 °C, given in Table 1, by combining an olivine with $X_{\text{Fe}}^{\text{Ol}}=0.5$ with an Fe–Mg biotite with molar Si:Al=3:1 and $X_{\text{Fe}}^{\text{Bt}}=0.3$, which is the equilibrium composition of biotite co-existing with olivine at this temperature (Fig. 1a). The resulting P – T pseudosection (not shown), computed with *Perple_X* and *our biotite model*, shows biotite + olivine + kalsilite as stable phases in roughly equal molar amounts above 730 °C up to 900 °C (at $P=1.1$ kbar). The predicted Al^{VI} level in biotite is zero confirming the in part-I discussed evidence of no Tschermak components in biotites in the exchange experiments of Zhou (1994). The use of the olivine–biotite exchange reaction to calibrate the Fe–Mg part of the model has a considerable benefit compared to, e.g., the garnet–biotite exchange experiments, where the Mg–Fe interaction in biotite is affected by a considerable amount of octahedral Al (see below).

Table 1 Bulk compositions (molar) used in the construction of pseudosections with *Perple_X* and in the calculation of mineral–chemical data given in Table 2

Bulk molar	SiO ₂	Al ₂ O ₃	FeO	MgO	K ₂ O	X _{Fe}	References ^a	Bulk used in text	Solution models considered in <i>Perple_X</i> calculation ^b
Bt:Ol=1:1 molar	41.67	8.33	15.83	25.83	8.33	0.38	[1]		Bt, Ol, Opx, Grt, Ph, Crd, St, Spl, Ctd, Chl
Alm90–Ann50 ^c	42.857	14.143	38.229	4.629	0.143	0.892	[2]	Table 1, Figs. 3, 4	Bt, Grt, Opx, Ol, Spl, Ph, Ctd
Alm90–Ann75 ^c	42.857	14.143	38.443	4.414	0.143	0.897	[2]	Table 1	Bt, Grt, Opx, Ol, Spl, Ph, Ctd
Alm90–Ann100 ^c	42.857	14.143	38.657	4.200	0.143	0.902	[2]	Table 1	Bt, Grt, Opx, Ol, Spl, Ph, Ctd
Alm80–Ann40 ^d	42.857	13.929	33.429	9.429	0.357	0.780	[3]	Figures 4, 5	Bt, Grt, Opx, Ol, Spl, Ph, Ctd
Alm70–Ann25 ^d	42.857	13.929	29.036	13.821	0.357	0.678	[3]	Figures 4, 5	Bt, Grt, Opx, Ol, Spl, Ph, Ctd
T–X pseudosection	42.857	14.143	21.429–42.857	21.429–0.000	0.143	0.5–1.0		Figure 6	Bt, Grt, Opx, Ol, Spl, Crd, Ph, Ctd, St, Chl
T–X pseudosection	42.857	14.143	25.714–42.857	17.143–0.000	0.143	0.6–1.0		Figures 7, 8	Bt, Grt, Opx, Ol, Spl, Ph, Ctd
Bt:Grt:Crd=2:1:1 ^e	46.767	16.986	13.281	19.784	3.182	0.402	[4]	Figure 9	Bt, Grt, Crd, Opx, Ol, Spl
Average metapelite ^f	68.76	9.87	7.64	4.01	3.16	0.66	[5]	Figure 10	Bt, Grt, Ph, Crd, Ctd, St, Chl, Opx, Melt
T–X pseudosection	68.76	9.87	0.00–11.65	11.65–0.00	3.16	0.0–1.0		Figure 11	same as for Figure 10
High-grade metapelite ^g	57.48	19.86	14.36	6.19	2.11	0.70	[6]	Figure 13	Bt, Grt, Crd, Spl, Ph, Opx, Melt, St, Chl, Ctd
High-P metapelite ^h		34.29	29.97	23.32	12.41	0.56	[7]	Figure 14	same as Figure 13 + Tlc, Carp

^a[1] Zhou (1994); [2] Ferry and Spear (1978); [3] Gessmann et al. (1997); [4] Perchuk and Lavrent'eva (1983, Table 2); [5] White et al. (2014, Table 2); [6] Pitra and de Waal (2001, Table 1), sample X567, cited in Tajčmanova et al. (2009, their Fig. 2); [7] Wei and Powell (2003, sample M4)

^bBt biotite, Ol olivine, Opx orthopyroxene, Grt garnet, Ph phengite (white mica), Crd cordierite, St staurolite, Spl spinel, Ctd chloritoid, Chl chlorite, Tlc talc, Carp carpholite. Bt was Bt (D) in case of *our calculation*, or Bi (W) for a *W14 calculation*, other models were Grt (W), Crd (W), Opx (W), Mica (W), Ctd (W), St (W), Chl (W), Melt (W), and (W) model set from White et al. (2014), O (HP) from Holland and Powell (2011), Spl (WPC) from White et al. (2002), Tlc (ideal), and Carp (ideal). Besides solution models the following endmembers were considered: and (andalusite), sill (sillimanite), ky (kyanite), sa (sanidine), and qz (quartz). Solid solutions start with a capital letter, and pure phases are written in lowercase. Unless stated otherwise, the calculations where done under water-saturated conditions

^cMolar Grt:Bt ratio was 98:2, Fe/(Fe+Mg) in garnet in these experiments thus remained (nearly) unchanged due to garnet's large modal amount. Ann50 = Ann₅₀Phl₅₀, Ann75 = Ann₇₅Phl₂₅, Ann100 = Ann₁₀₀Phl₀, Alm90 = Alm₉₀Py₁₀, Alm80 = Alm₈₀Py₂₀, Alm70 = Alm₇₀Py₃₀

^dWeight Grt:Bt ratio was 95:5 in these experiments

^eWeight ratio

^fSuprasolidus conditions modeled with a fixed bulk H₂O content of 6.56 mol%, which was the water content which replicated the wet solidus calculated under water-saturated conditions

^gSuprasolidus conditions modeled with a fixed bulk H₂O content of 7.00 mol%, which was the water content which replicated the wet solidus calculated under water-saturated conditions

^hCalculated under quartz saturated conditions

Biotite–orthopyroxene

The calculation of the Fe–Mg distribution between biotite and orthopyroxene and comparison with experimentally determined distribution coefficients (K_D s) constitutes an independent test on the validity of biotite properties derived in the companion paper. This exchange, given by the reaction:

which was experimentally studied by Fonarev and Konilov (1986) at $P = 4.9$ kbar, T 's of 700, 750, and 800 °C and $\log_{10} f_{\text{O}_2}$ conditions dictated by the quartz–fayalite–magnetite (QFM) oxygen fugacity (f_{O_2}) buffer. Whereas biotite from the run products was found to be homogeneous, orthopyroxene was notably inhomogeneous, comprising unreacted starting compositions, intermediate metastable, and evolved possible equilibrium compositions. Fonarev and Konilov (1986) applied a complex statistical treatment to the whole set of their experimental data to establish equilibrium relations and to define mineral compositions that likely represent equilibrium. If their experiments indeed successfully bracketed equilibrium Fe–Mg distributions remains an open question. Their data at $T = 700$ °C are shown in Fig. 2 including calculated distribution curves based on *our* and *W14 calculations*. Both types of calculations represent the experimental data within error. For a given $X_{\text{Fe}}^{\text{Opx}}$, however, *our biotite model* yields a 0.05–0.1 lower mole fraction $X_{\text{Fe}}^{\text{Bt}}$. This also holds for the other isothermal Roozeboom plots in the Supplementary Materials.

Biotite–garnet

The biotite–garnet exchange reaction constitutes yet another independent test on the validity of biotite properties derived in the companion paper.

The experiments of Ferry and Spear (1978) Using synthetic starting materials, Ferry and Spear (1978–FS78) undertook the first experimental study of the partitioning of Fe and Mg between biotite and garnet, given by the reaction:

at $P = 2.07$ kbar, T 's between 550 and 800 °C (spaced in ~ 50 °C intervals) and oxygen fugacity buffered by the graphite–methane buffer. Because their exchange experiments were conducted with a very high molar garnet:biotite ratio (98:2), garnet composition ($\text{Alm}_{90}\text{Py}_{10}$ and $\text{Alm}_{80}\text{Py}_{20}$) remained unchanged during the experiments, which was also proven by microprobe analysis from the run products. Equilibrium was demonstrated by performing two experiments at each T , in which starting biotite had either a more Mg-rich

or a more Fe-rich composition than biotite in equilibrium with garnet at this T ($X_{\text{Fe}}^{\text{Bt}}$ in these starting biotites was 0.25, 0.5, 0.75, or 1.0). After the experiment, run products were dispersed on polished diamond surfaces, and biotite compositions were measured with a microprobe using a linear relationship between Fe and Mg X-ray intensities and concentrations (see FS78 for more details). Thus, only the Fe and Mg contents of reacted biotite grains were measured, whereas there is no information on the content of possible Al^{VI} in biotite. Six compositional brackets were determined in such a way by FS78 through experiments with $\text{Alm}_{90}\text{Py}_{10}$ garnet. The equilibrated biotites were found to differ not more than 0.04 in their final $X_{\text{Fe}}^{\text{Bt}}$ mole fractions (FS78 give an accuracy of ± 0.01 for $X_{\text{Fe}}^{\text{Bt}}$). As a result of increasing experimental temperatures from 550 to 800 °C, their $X_{\text{Fe}}^{\text{Bt}}$ rose from values around 0.61–0.75, which is a change of ca. 0.15 in mole fraction $X_{\text{Fe}}^{\text{Bt}}$ for this temperature interval of 250 °C. Two wider brackets were obtained by FS78 in experiments using $\text{Alm}_{80}\text{Py}_{20}$.

We have reconstructed bulk compositions for the FS78 experiments, based on the molar 98:2 garnet:biotite ratio they have used ($\text{Alm}_{90}\text{Ann}_{50}$, $\text{Alm}_{90}\text{Ann}_{75}$, and $\text{Alm}_{90}\text{Ann}_{100}$, Table 1) and have calculated the equilibrium compositions of biotite and garnet at the experimental temperatures and a pressure of 2.07 kbar using *Perple_X* and *Theriak* software and *our* and *W14* biotite thermodynamic data and solution models (note that for garnet $W_{\text{AlmPy}} = 2.5$ kJ/mol in all calculations). The results are given in Table 2 and are plotted in Fig. 3 for the case of bulk composition $\text{Alm}_{90}\text{Ann}_{50}$. From Fig. 3a, which shows $X_{\text{Fe}}^{\text{Bt}}$ and Al^{VI} in biotite as a function of temperature, it can be seen that the *our calculations* reproduce the experimentally determined $X_{\text{Fe}}^{\text{Bt}}$ of FS78 well within error. The *W14 calculation* fails to do so, it predicts a ca. 0.1 mol fraction too large $X_{\text{Fe}}^{\text{Bt}}$. As a consequence, $\ln K_D^{\text{this-study}}$, where $K_D = (\text{Mg/Fe})^{\text{Grt}}/(\text{Mg/Fe})^{\text{Bt}}$, is consistent with all FS78 experimental $\ln K_D$ -brackets, whereas $\ln K_D^{\text{W14}}$ is systematically lower outside the 2σ error range of the data (Fig. 3b). Both biotite models indicate an Al^{VI} content in biotite in the order of 0.2–0.4 apfu. However, Al^{VI} is predicted to decrease with T by an *our calculation* and to increase with T by a *W14 calculation* (note that computed Al^{VI} corresponds to the Tscherma substitution-balanced octahedral Al, i.e., $\text{Al}^{\text{VI}} = \text{Al}^{\text{IV}} - 1$).

The volume % garnet and biotite computed by *Perple_X* and *Theriak* for the experimental bulk compositions are quite similar. They amount to 1.4–2.7 vol% biotite and 96.5–96.9 vol% garnet. Additional phases predicted to be stable with biotite + garnet are orthopyroxene, olivine, quartz, and sanidine/spinel in the high- T runs. If present indeed, they were undetectable due to their predicted small amounts < 1 vol% (Table 2).

Table 2 Compositions of KFMASH-biotite and -garnet computed with the software *Perple_X* (Connolly 2005, 2009—Perp) and *The-riak-Domino* (de Capitani and Brown 1987—TD) for bulk compositions used by Ferry and Spear (1978—FS78) in their experimental

study of the Fe/Mg exchange between garnet and biotite at $P=2.07$ kbar (molar garnet/biotite ratio was 98/2, and garnet Fe/Mg ratio was 9/1 in the experiments and assumed to remained unchanged)

T [°C]	Soft- ware	Bulk ^a	Biotite					Garnet		$\ln K_D$			Vol%		
			X_{Fe}		Al^{VI}			X_{Fe}		—			—		
			FS78	This study	W14	This study	W14	This study	W14	FS78	This study	W14	Biotite	Garnet	Other ^b
550	Perp	Ann75	0.620	0.615	0.704	0.346	0.177	0.904	0.902	−1.741	−1.773	−1.347	2.6	96.5	Opx(0.9)
	TD			0.609	0.700	0.345	0.162	0.903	0.902		−1.786	−1.370	2.6	96.5	Ol(0.7)qz(0.2)
550	Perp	Ann50	0.587	0.603	0.691	0.350	0.182	0.899	0.897	−1.811	−1.766	−1.357	2.6	96.5	Opx(0.9)
	TD			0.597	0.685	0.345	0.166	0.898	0.897		−1.783	−1.385	2.6	96.5	Ol(0.7)qz(0.2)
599	Perp	Ann75	0.645	0.646	0.734	0.318	0.192	0.903	0.901	−1.623	−1.626	−1.193	2.6	96.5	Opx(0.9)
	TD			0.643	0.729	0.327	0.179	0.902	0.901		−1.633	−1.219	2.6	96.8	Ol(0.5)qz(0.1)
599	Perp	Ann50	0.608	0.635	0.720	0.322	0.196	0.898	0.896	−1.728	−1.622	−1.209	2.6	96.6	Opx(0.8)
	TD			0.632	0.716	0.328	0.183	0.897	0.896		−1.629	−1.232	2.6	96.5	Opx(0.9)
651	Perp	Ann75	0.679	0.675	0.758	0.296	0.209	0.902	0.900	−1.459	−1.491	−1.060	2.6	96.6	Opx(0.8)
	TD			0.675	0.754	0.295	0.198	0.902	0.900		−1.490	−1.084	2.6	96.5	Opx(0.9)
651	Perp	Ann50	0.661	0.665	0.747	0.298	0.213	0.897	0.896	−1.497	−1.482	−1.069	2.6	96.6	Opx(0.8)
	TD			0.664	0.742	0.297	0.202	0.897	0.896		−1.486	−1.095	2.6	96.5	Opx(0.9)
698	Perp	Ann75	0.704	0.696	0.777	0.280	0.227	0.902	0.900	−1.342	−1.389	−0.951	2.7	96.6	Opx(0.7)
	TD			0.698	0.772	0.281	0.217	0.902	0.900		−1.377	−0.978	2.7	96.6	Opx(0.7)
698	Perp	Ann50	0.690	0.686	0.767	0.282	0.230	0.897	0.895	−1.353	−1.379	−0.951	2.7	96.6	Opx(0.7)
	TD			0.688	0.761	0.283	0.220	0.897	0.895		−1.372	−0.988	2.6	96.5	Opx(0.9)
749	Perp	Ann50	0.695	0.706	0.781	0.269	0.250	0.895	0.895	−1.330	−1.273	−0.873	1.9	96.9	Ol(0.7)sa(0.5)
	TD			0.707	0.778	0.308	0.243	0.895	0.895		−1.260	−0.887	1.9	96.9	Ol(0.7)sa(0.5)
738	Perp	Ann100	0.730	0.720	0.800	0.269	0.238	0.904	0.905	−1.271	−1.301	−0.866	2.0	96.9	Ol(0.6)sa(0.5)
	TD			0.723	0.796	0.306	0.231	0.905	0.905		−1.292	−0.890	1.9	96.9	Ol(0.7)sa(0.5)
799 ^c	Perp	Ann50	0.710	0.721	0.795	0.273	0.262	0.894	0.895	−1.258	−1.185	−0.780	1.4	96.6	Ol(1.0)Spl(0.1)sa(0.9)
	TD			0.725	0.792	0.306	0.248	0.895	0.895		−1.170	−0.804	1.9	96.9	Ol(0.7)sa(0.5)
799 ^c	Perp	Ann100	0.750	0.740	0.812	0.281	0.251	0.904	0.903	−1.155	−1.197	−0.773	1.9	96.9	Ol(0.7)sa(0.5)
	TD			0.744	0.811	0.312	0.239	0.904	0.904		−1.179	−0.790	1.9	96.9	Ol(0.7)sa(0.5)

The $\ln K_D$ of this exchange as well as computed volume % of minerals are given. In the calculations, the KFMASH-biotite activity model and thermodynamic standard-state data of annite, phlogopite, and eastonite of *this study* (part-I) were used. The activity model for KFMASH-garnet and all other thermodynamic data were those cited in White et al. (2014—W14). Analogous calculations with all thermodynamic data and activity models according to W14, are listed for comparison. The relevant T – X pseudosections are shown in Figs. 6, 7 and 8

$X_{Fe} = Fe/(Fe + Mg)$; Al^{VI} = octahedral Al (apfu, 12 oxygen formula)

^aBulk compositions are given in Table 1

^bOpx orthopyroxene, qz quartz, Ol olivine, sa sanidine, Spl spinel

^cCalculated at 2.7 kbar, as garnet + biotite are no longer stable at 2.07 kbar at this T

The experiments of Gessmann et al. (1997) Gessmann et al. (1997—G97) extended the FS78 work to more Mg-rich bulk compositions, by conducting the same type of exchange experiments (high garnet:biotite weight ratio of 95:5) with Alm₈₀Py₂₀ and Alm₇₀Py₃₀ garnet starting compositions, X_{Fe}^{Bt} starting compositions of 0.25, 0.4, 0.5, and 0.65, at the same pressure of $P=2.07$ kbar and T 's ranging between 600 and 800 °C. They characterized garnet and biotite in their run products more comprehensively than FS78 by not only tabulating X_{Fe}^{Bt} , but also its Al^{VI} content and X_{Fe}^{Grt} . Similar

to FS78, garnet composition remained nearly unchanged to within 0.02 mol fraction after the conclusion of an exchange experiment. The composition of biotite in G97 experiments in terms of X_{Fe}^{Bt} , equilibrated with either Alm₈₀Py₂₀ or Alm₇₀Py₃₀ garnets, is shown in Fig. 4a as a function of temperature. For comparison, the FS78 data from Table 1 are also plotted. As discussed by G97, their high- T Alm₇₀Py₃₀ data bear inconsistencies, which is obvious from the fact that, e.g., at 800 °C, X_{Fe}^{Bt} is larger than that of biotite equilibrated with Alm₈₀Py₂₀. At a given T , X_{Fe}^{Bt} in equilibrium

Fig. 3 Plot of the experimental data of Ferry and Spear (1978, FS78) on the Fe–Mg exchange between biotite and garnet ($P = 2.07$ kbar). The experimentally determined molar Fe/(Fe + Mg) content of biotite ($X_{\text{Fe}}^{\text{Bt}}$) in equilibrium with garnet of Alm90Py10 composition is shown in **a** as open and filled squares (depending if the equilibrium was approximated from oversaturated or undersaturated conditions) as a function of temperature. *Perple_X* modeled $X_{\text{Fe}}^{\text{Bt}}$ from *our calculation* (experimental bulk composition Alm90–Ann50 given in Table 1) is drawn as solid line. Broken line is an analogous *W14 calculation*: predicted Al^{VI} (apfu) of biotite as a function of temperature is also shown. The modeled temperature dependence of $\ln K_D$ of the garnet–biotite Fe–Mg exchange and computed with *Perple_X* is plotted in **b** for both cases of a *this study* (solid line) and a *W14 calculation* (broken line). Error bars of experimental $\ln K_D$ values are $\pm 2\sigma$

with Alm₇₀Py₃₀ should be, however, systematically lower compared to $X_{\text{Fe}}^{\text{Bt}}$ in equilibrium with Alm₈₀Py₂₀ (see G97 for further discussion and possible explanations for the deviation of their high- T Alm₇₀Py₃₀ runs). The Al^{VI} content of biotite is shown in Fig. 4a (lower part), and experimental $\ln K_D$ values of G97, and FS78 for exchange reaction (3) are plotted in Fig. 4b as a function of temperature. The experimental record shows that $\ln K_D$ gets less negative, i.e., K_D increases with increasing bulk- X_{Mg} content.

Similar as in the case of FS78 described above, bulk compositions were computed for the G97 experiments (Alm₈₀–Ann₄₀ and Alm₇₀–Ann₂₅, Table 1) and phase relationships determined with *Perple_X* using *our* and

W14 calculations. The predicted mineral compositions and $\ln K_D$ from *our calculation* are shown as curves in Fig. 4 to allow a comparison to the experimental values, those for the *W14 calculation* in Fig. 5. In both figures, the results from Alm₉₀–Ann₅₀ (bulk in FS78 experiments) are also included.

The following features are noticeable from the results of *our calculations*: For bulk Alm₈₀–Ann₄₀, $X_{\text{Fe}}^{\text{Bt}}$ is larger by ca. 0.05 mol fractions than most experimental values, and for Alm₇₀–Ann₂₅, the agreement is good (except for the high- T data as mentioned above, Fig. 4a). The predicted Al^{VI} content in biotite matches the measured ones above 700 $^{\circ}\text{C}$ and is somewhat larger at lower T s. It decreases slightly with

Fig. 4 **a** $X_{\text{Fe}}^{\text{Bt}}$ in equilibrium with garnet of Alm90Py10 composition (red; Ferry and Spear 1978, FS78), or of Alm80Py20 (blue) and Alm70Py30 composition (dark yellow; Gessmann et al. 1997, G97), i.e., color codes indicate subsequent lower X_{Mg} bulk compositions, as a function of temperature. Corresponding experimental $\ln K_{\text{D}}$ s are shown in **b** with error bars (2σ) for the Alm70Py30 experiments. The Al^{VI} content of biotite, measured by G97 in their Alm80Py20 and Alm70Py30 experiments with a microprobe, is shown as black dots in the lower part of **a**. Solid lines are *Perple_X*-computed $X_{\text{Fe}}^{\text{Bt}}$, Al^{VI} , or $\ln K_{\text{D}}$ from our calculations using bulk compositions of experiments, as given in Table 1. The colors of the lines indicate to which experimental data the fit corresponds to

Fig. 5 Same caption as in Fig. 4, except that solid lines represent *W14* calculations

Fig. 6 T - $X_{\text{FeO}/(\text{FeO} + \text{MgO})}$ pseudosection computed at $P=2.07$ kbar with *Perple_X* (this study calculation in the KFMASH system, H_2O in excess, bulk given in Table 1), relevant to illustrate phase relations in the Fe–Mg exchange experiments between biotite and garnet of Ferry and Spear (1978, FS78) and Gessmann et al. (1997, G97). Purple vertical lines indicate the experimental bulk compositions. Note that cordierite bearing assemblages would be stable in G97 bulks. The color of phase assemblage fields indicates the thermodynamic variance of the equilibria. White = divariant fields, light gray = trivariant, and dark gray = quadrivariant. Adjacent fields always differ by at least one phase. In other words, adjacent fields always differ in their variance by one degree of freedom. Therefore, adjacent fields, which have the same color, have thin fields in between them containing both phases which differ in the adjacent fields. For example, in the case of adjacent divariant fields, a univariant reaction line separated the two fields. Fields separated by a point differ by two phases. These phase diagram rules apply for all subsequent pseudosections (Figs. 7, 8, 10, 11, 13, 14)

rising temperatures and increases with increasing X_{Mg} of the bulk composition, i.e., experiments with Alm70 have higher Al^{VI} than experiments with Alm80. Computed $\ln K_{\text{D}}^{\text{this-study}}$ values agree within error with experimental ones for bulk Alm80–Ann40, whereas for bulk Alm70–Ann25, this is only the case at 600 °C. A slight dependence of $\ln K_{\text{D}}^{\text{this-study}}$ on bulk composition is visible in the form that it gets less negative (i.e., K_{D} increases with increasing bulk X_{Mg}).

The most obvious differences of *W14-calculated* to experimental mineral–chemical data of biotite (Fig. 5) are the following: The agreement of $X_{\text{Fe}}^{\text{Bt}}$ with experimental

values is good only for bulk Alm70–Ann25 (Fig. 5a), but gets increasingly poor for Alm80–Ann40 and especially for Alm90–Ann50 (FS78 experiments, as already discussed above). The same applies accordingly for $\ln K_{\text{D}}^{\text{W14}}$, and its dependence on bulk- X_{Mg} is the reverse of that noticed above for *our calculations* (Fig. 5b). The predicted Al^{VI} content is in good agreement with the measured ones.

T - X_{Fe} pseudosection for FS78 and G97 experiments In Fig. 6, we present a T - X_{Fe} pseudosection at $P=2.07$ kbar (*our calculation* with *Perple_X*, no phases excluded except ortho-

amphibole), with molar $X_{\text{Fe}}^{\text{bulk}} = \text{FeO}/(\text{FeO} + \text{MgO})$ ranging between 0.5 and 1.0 and temperatures from 550 to 800 °C to illustrate computed phase relations relevant for the FS78 and G97 exchange experiments ($X_{\text{Fe}}^{\text{bulk}}$ in FS78 and G97 is shown as vertical purple lines). The pseudosection shows that FS78 experimented in a range where biotite + garnet are stable at most T 's co-existing with orthopyroxene (in small amounts < 1 vol%, Table 2). At lowest T , chlorite (Chl) and at temperatures above ~750 °C, cordierite (Crd), olivine, sanidine, and spinel would be additionally stable. For the bulk compositions used by G97, on the other hand, cordierite is predicted at most T 's, +chlorite up to ca. 610 °C, to coexist with garnet + biotite. Because both minerals were not reported—the computed vol% of cordierite between 20 and 50 vol% in the high- T experiments, and 10–5 vol% chlorite for the low- T experiments should have been detected by XRPD—it can be assumed that kinetic factors inhibited the growth of both minerals in the experimental charges within the time-scale of the experiments. Similarly, Berman et al. (2007), based on phase-stability calculations with *Theriak-Domino*, noted that their experimental mineral assemblage biotite + sillimanite + sanidine + quartz is metastable with respect to cordierite + sanidine.

If cordierite, chlorite, staurolite, and orthoamphibole are excluded, a T - X_{Fe} pseudosection results as shown in Fig. 7a (*our calculation*). The biotite + garnet + orthopyroxene field extends to lower bulk- X_{Mg} , covering now also G97 experiments with Alm₈₀Py₂₀ (bulk Alm₈₀–Ann₄₀ in Table 1). For bulk Alm₇₀–Ann₂₅, low-variance 5-phase assemblages are predicted with garnet + biotite + orthopyroxene ± additional spinel, andalusite, or quartz. Noteworthy, biotite is not stable for this bulk composition at 800 °C, which might explain the deviation of experimental high- T $\ln K_D$ values from the $\ln K_D$ vs. T trend as defined by the lower temperature experimental data (Fig. 5b, G97, their Fig. 11). Compared to the high-variance 3-phase garnet + biotite + orthopyroxene field, where vol% orthopyroxene is very low (< 1 vol%) and thus experimentally not detectable, the amount of orthopyroxene for the Alm₇₀–Ann₂₅ bulk composition is much larger (20–40 vol%), which is consistent with the observation of G97 that orthopyroxene needles appear in their high- T runs for this bulk composition.

Isopleths for $X_{\text{Fe}}^{\text{Bt}}$ and Al^{VI} in biotite are also plotted in the T - X_{Fe} pseudosection of Fig. 7a. $X_{\text{Fe}}^{\text{Bt}}$ isopleths are relatively steep, so that, as observed in the FS78 experiments, $X_{\text{Fe}}^{\text{Bt}}$ increases by only ~0.13 mol fractions over the whole temperature range from 550 to 800 °C. The mole fractions $X_{\text{Fe}}^{\text{Bt}}$ as measured in the FS78 experiments are indicated as purple numbers next to the purple vertical line, which indicates the bulk composition of the experiments. These $X_{\text{Fe}}^{\text{Bt}}$ are the mean of the equilibrium brackets of FS78 (exact experimental $X_{\text{Fe}}^{\text{Bt}}$ values are also mentioned in Table 2). Comparison of the calculated $X_{\text{Fe}}^{\text{Bt}}$ isopleths with

these experimental values provides a direct test for internal consistency with the FS78 experiments. Figure 7a shows the near perfect agreement of *our calculation* in terms of $X_{\text{Fe}}^{\text{Bt}}$.

There exists a considerable debate on the likely Al^{VI} content of biotite in FS78 experiments (see Holdaway 2000, and discussion therein). FS78 themselves suppose that approximately 6% of octahedral cations in their synthetic Ann₁₀₀ could be Al. The Al^{VI} isopleths have a negative slope in the garnet + biotite + orthopyroxene 3-phase field, and Al^{VI} is predicted to decrease with increasing T for a given bulk composition. This means that FS78 biotites were very likely (a) not as Al-rich as those analyzed by G97, (b) not Al^{VI} -free nor contained only minor Al^{VI} , as assumed in various works analyzing the garnet–biotite exchange data (e.g., Kleemann and Reinhardt 1994; Powell and Holland 1999; Holdaway 2000), but incorporated octahedral Al in the order of 0.25–0.35 apfu (Fig. 4a, Table 1). This conclusion holds also based on a *W14 calculation* for which the predicted Al^{VI} level would be around 0.2 apfu for FS78 biotites (Fig. 5a, Table 1).

We have also calculated the equivalent pseudosection of Fig. 7a with an alternative version of *our biotite* model, which uses a single symmetric interaction parameter to describe the enthalpy of mixing behavior along the Ann–Phl binary instead of two interaction parameters as in our original asymmetric model. As shown in part-I, assuming a symmetric interaction parameter in the single inversion least-squares procedure to derive calibrated parameters for our biotite model also leads to changes in $\Delta H_{\text{f,Ann}}^{\circ}$. The pseudosection calculated with this $\Delta H_{\text{f,Ann}}^{\circ} = -5136.7 \pm 2.1$ kJ/mol and $W_{\text{AnnPhl}}^{\text{G}} = 9.3 \pm 1.8$ kJ/mol (3-site cation basis) is shown in Fig. 7b and indicates that a symmetric model has $X_{\text{Fe}}^{\text{Bt}}$ isopleths, which disagree with the experimental $X_{\text{Fe}}^{\text{Bt}}$ in the order of 0.1 molar fraction. To achieve consistency with the experimental data of FS78 on the Fe–Mg distribution between biotite and garnet, one needs to apply a rather unrealistically large non-ideality for Fe–Mg mixing in garnet ($W_{\text{AlmPy}}^{\text{G}}$ around 12 kJ/mol, 3-site cation basis). Therefore, this symmetric model is not internally consistent with FS78 and not further considered in this paper.

We have used a $W_{\text{FaFo}}^{\text{G}} = 5$ kJ/mol (one-site basis) in our single inversion least-squares procedure to derive parameters for biotite from the thermodynamic analysis of the biotite–olivine Fe–Mg exchange data of Zhou (1994). However, the studies of Sack (1980) and Sack and Ghiorso (1989) point to a larger Fe–Mg non-ideality in olivine of $W_{\text{FoFa}}^{\text{G}}$ around 10 kJ/mol (one-site basis). In part-I, we have used this mixing parameter of olivine to derive two alternate biotite models, one with symmetric and the other with asymmetric Fe–Mg mixing in biotite. The symmetric model has a $W_{\text{PhlAnn, sym}}^{\text{G}} = 26.0 \pm 1.7$ kJ/mol and an associated different $\Delta H_{\text{f,Ann}}^{\circ} = -5142.7 \pm 2.10$ kJ/mol. For the asymmetric

case, $W_{\text{PhlAnn}}^{\text{G}} = 0.9 \pm 6.1$ kJ/mol, $W_{\text{AnnPhl}}^{\text{G}} = 36.4 \pm 2.4$ kJ/mol, and the associated $\Delta H_{\text{f,Ann}}^{\circ} = -5136.2 \pm 1.7$ kJ/mol.

Figure 7c, d shows the pseudosections, equivalent to Fig. 7a, computed with these alternate biotite models (calibrated with $W_{\text{FoFa}}^{\text{G}} = 10$ kJ/mol, one-site basis). The $X_{\text{Fe}}^{\text{Bt}}$ isopleths of both these models show considerable disagreement with the experimental $X_{\text{Fe}}^{\text{Bt}}$ and are therefore not considered to be consistent with the FS78 experiments. Even when one changes $W_{\text{AlmPy}}^{\text{G}}$, no agreement closer than 0.1 molar fraction to the experimental value can be found. These biotite models, based on $W_{\text{FoFa}}^{\text{G}}$ around 10 kJ/mol, are thus not further considered in this paper.

Finally, we compared *our biotite* model with the *W14* biotite model. The dependence of $\ln K_{\text{D}}$ of the garnet–biotite Fe–Mg exchange reaction (Eq. 3) on bulk composition is shown in Fig. 8, which is the same T – X_{Fe} pseudosection as drawn in Fig. 7a, but with contours of $\ln K_{\text{D}}$, computed for both cases of an *our* and a *W14 calculation*. In the low-variance fields, $\ln K_{\text{D}}$ is constant as a function of bulk composition and only temperature-dependent ($X_{\text{Fe}}^{\text{bulk}} < \text{ca. } 0.75$). In the high-variance fields toward more Fe-rich bulk compositions, $\ln K_{\text{D}}$ contours become increasingly convex in case of *our calculations* which means that $\ln K_{\text{D}}$ values get less negative with increasing bulk X_{Mg} at constant temperature, in accordance with the experimental evidence. For the FS78 bulk composition, the experimentally determined $\ln K_{\text{D}}$ values of FS78 (Table 2, Fig. 3b) can be directly read from the $\ln K_{\text{D}}$ isopleths in Fig. 8. From the computed bulk composition dependence of $\ln K_{\text{D}}$, which can be seen in Fig. 8, it is also clear that the calibration of FS78 will overestimate temperatures when applied to more Mg-rich bulks compared to the experimental one when such a bulk compositional effect is not considered. A $\ln K_{\text{D}}$ of -1.4 , for example, means a temperature of ca. 675 °C for the FS78 bulk composition (at 2.07 kbar), but corresponds to a by ca. 23 °C lower temperature when bulk X_{Mg} increases by ca. 0.1 mol fractions (Fig. 8). It is thus not surprising that it was noted in the literature that the FS78 calibration appears to overestimate metamorphic temperatures (e.g., Chipera and Perkins 1988; Kleemann and Reinhardt 1994). The effect of retrograde net transfer equilibria on garnet–biotite geothermometry could also play a role, but was not considered in these papers.

The $\ln K_{\text{D}}$ isopleths from a *W14 calculation* are nearly similar to those obtained from *our calculations* in the low-variance fields at $X_{\text{Fe}}^{\text{bulk}} < \text{ca. } 0.75$. At more Fe-rich bulk compositions, however, $\ln K_{\text{D}}$ contours take a concave form and predict $\ln K_{\text{D}}$'s inconsistent with the experimental data of FS78 and the bulk composition dependence of the distribution coefficient (Fig. 4b).

The experiments of Perchuk and Lavrent'eva (1983) Perchuk and Lavrent'eva (1983—PL83) studied the Fe–Mg exchange equilibria between cordierite, garnet, and biotite

experimentally using mostly natural starting materials at $P=6$ kbar and T 's from 575 to 950 °C and f_{O_2} as defined by the Nickel–Nickel-oxide buffer. The large number of experiments over a wide range of Fe–Mg mineral compositions ($X_{\text{Mg}}^{\text{Grt}}=0.05$ – 0.76 , $X_{\text{Mg}}^{\text{Bt}}=0.22$ – 0.83) is a major benefit of their work. A drawback is, however, that their natural run products, with grain sizes of up to 300 μm , were strongly zoned. Equilibrium between biotite and garnet was approached by experiments with starting compositions on opposite sides of the Fe–Mg distribution curve, and the most shifted compositions were assumed to represent equilibrium values (see PL83 for more details on their method to estimate equilibrium compositions). A further complication in their experiments is the fact the natural minerals used for the study contained CaO and MnO in the order of up to 4 wt% in the case of garnet and TiO_2 (1–2 wt%) in the case of biotite. The Al content of equilibrated biotites were not measured by PL83, but were so at a later stage by Aranovich et al. (1989) for a subset of the PL83 biotites (their Table 2, 27 data). The Al level in these biotites is rather uniform, with Al^{VI} in the range 0.32–0.42 apfu (Fig. 9b). The resulting $\ln K_{\text{D}}$ of the garnet–biotite equilibrium is plotted as a function of temperature in Fig. 9a, including 2σ -error bars, calculated based on the assumption that measured mole fractions of garnet and biotite have a 2σ -error of 0.02.

In their experiments conducted at 700 °C, PL83 used a weight ratio of biotite:garnet:cordierite = 2:1:1. From the data given in Tables 2 and 6 on the chemistry of starting materials, we have constructed a bulk composition that should represent at least part of their numerous 700 °C runs. With an $X_{\text{Fe}}^{\text{bulk}} = 0.4$, it is more Fe-poor than the exchange experiments of FS78 and G97 (Table 1). At $P=6$ kbar, the computed P – T pseudosection *our calculation* with *Perple_X*, excluding chlorite, staurolite, orthoamphibole and chloritoid) shows a garnet–biotite–cordierite 3-phase field between 660 and 800 °C. Additionally, minor amounts of spinel and quartz (< 1 vol%) are predicted at higher and lower T 's, respectively, indicating that the experimentally studied garnet + biotite + cordierite assemblage is stable at the P – T conditions applied by PL83. The predicted Al^{VI} content of biotite in the biotite–garnet–cordierite assemblage from *our calculations* is in good agreement with the measured values up to 800 °C and somewhat lower for the highest temperature data (Fig. 9b). Modeled $\ln K_{\text{D}}$ for both *our* and a *W14 calculation* is very similar when plotted against temperature (Fig. 9a). The $\ln K_{\text{D}}$ vs. T slope is, however, flatter than the experimental trend, so that agreement with the experimental K_{D} 's is poor above ~ 800 °C. We also tested another bulk composition, namely that in the 900 °C runs of PL83, where the biotite:garnet:cordierite weight ratio was 3:1:1 and found the same result, i.e., their highest- T brackets could not be reproduced by *our* nor by a *W14 calculation*.

Pseudosection of an average metapelite

White et al. (2014) have constructed a P – T pseudosection for an average metapelite bulk composition in the KFMASH system. We have adopted their model pelite bulk composition (Table 1) and compared the P – T pseudosection resulting from *our* with an analogous *W14 calculation* in Fig. 10a, b

(see also *W14*, their Fig. 4). As already outlined above, the difference in topologies is thus merely the effect of using *our biotite activity model* (Table 8, part-I), as well as thermodynamic data of biotite endmembers from part-I (Table 9), all other data being the same. Generally, the change in topology is not very pronounced. Noteworthy is that high-pressure stability fields are shifted to somewhat lower

Fig. 7 T - $X_{\text{FeO}/(\text{FeO} + \text{MgO})}$ pseudosection computed at $P=2.07$ kbar with *Perple_X* in the KFMASH system, with H_2O in excess (bulk given in Table 1). In contrast to Fig. 6, cordierite, chlorite, orthoamphibole and staurolite were excluded in this calculation. Isopleths are predicted Al^{VI} in biotite (colored lines) and $X_{\text{Fe}}^{\text{Bt}} = \text{Fe}/(\text{Fe} + \text{Mg})$ (broken lines). Bulk compositions in the Fe–Mg exchange experiments between biotite and garnet of Ferry and Spear (1978) and of Gessmann et al. (1997) are shown as vertical lines labeled FS78 and G97. For FS78 bulk, computed $X_{\text{Fe}}^{\text{Bt}}$ isopleths can be compared to experimentally determined $X_{\text{Fe}}^{\text{Bt}}$ (purple numbers). Pseudosections shown in **a** and **b** are calculated with Fe–Mg mixing properties of biotite as obtained from the thermodynamic analysis of Zhou (1994)'s olivine–biotite Fe–Mg exchange experiments, using a $W_{\text{FaFo}}^{\text{G}}$ of 5 kJ/mol, those in **c** and **d** of 10 kJ/mol (one-site basis). *Our preferred calculation* is pseudosection **a** with asymmetric Fe–Mg mixing in biotite ($W_{\text{PhlAnn}}^{\text{G}} = -8.8$ kJ/mol, $W_{\text{AnnPhl}}^{\text{G}} = 14.3$ kJ/mol, associated $\Delta H_{\text{f,Ann}}^{\circ} = -5131.6$ kJ/mol, Tables 7, 8, part-I). Pseudosection **b** was computed with symmetric ($W_{\text{AnnPhl}}^{\text{G}} = 9.3$ kJ/mol, associated $\Delta H_{\text{f,Ann}}^{\circ} = -5136.7$ kJ/mol), **c** with asymmetric ($W_{\text{PhlAnn}}^{\text{G}} = 0.9$ kJ/mol, $W_{\text{AnnPhl}}^{\text{G}} = 36.4$ kJ/mol, associated $\Delta H_{\text{f,Ann}}^{\circ} = -5136.2$ kJ/mol), and **d** with symmetric Fe–Mg mixing in biotite ($W_{\text{PhlAnn}}^{\text{G}} = 26.0 \pm 1.7$ kJ/mol, associated $\Delta H_{\text{f,Ann}}^{\circ} = -5142.7$ kJ/mol). In contrast to the examples in the other subfigures, the agreement between experimental and model $X_{\text{Fe}}^{\text{Bt}}$ is excellent in **a**

pressures based on *our calculations* (e.g., chlorite + phengite + quartz, biotite + garnet + phengite + quartz) and the high-temperature fields (e.g., cordierite + biotite + sanidine + quartz, biotite + sanidine + sillimanite + quartz) to lower temperatures. This makes the low-variance fields larger. Low-variance fields are good for thermobarometry, as the chemical potentials of the chemical components are fixed by the presence of the many co-existing phases. This means that the current biotite model can be used to more precisely estimate pressures and temperatures over a more extensive P , T range. Using the same model pelite composition, we also made a T - X_{Fe} pseudosection (*our calculation* at $P=6$ kbar, Fig. 11a). Low-variance fields involving garnet come in at $X_{\text{Fe}}^{\text{bulk}}$ of ca. 0.6–0.7 above ~ 570 °C, whereas more Fe-rich bulks ($X_{\text{Fe}}^{\text{bulk}}$ around 0.8–0.9) are required to stabilize these assemblages according to a *W14 calculation* (Fig. 11b). Note that Al^{VI} isopleths all become flat in the T - X pseudosection in the low-variance fields showing their independence on bulk composition. Considering isopleths of the Al^{VI} content in biotite from *our biotite model* (note that $\text{Al}^{\text{VI}} = \text{Al}^{\text{IV}} - 1$), these show an exponential drop at very Mg-rich compositions as a function of $X_{\text{Fe}}^{\text{bulk}}$ (in the range 0–0.2), i.e., Al^{VI} is extremely bulk X_{Fe} dependent, merging into flat, slightly negative slopes toward more Fe-rich bulks (with $X_{\text{Fe}}^{\text{bulk}} > \text{ca. } 0.4$). The isopleths of Al^{VI} increase with temperature (from ca. 0.2 apfu at low T 's), reach a value of ca. 0.43 at ca. 650 °C at maximum, and then decrease again. The trend of the Al^{VI} contours also predicts that the extent of the Tschermak substitution gets slightly larger going from Mg to Fe-rich biotites (as discussed in part-I, this seems to be related to the fact that biotites then have their 'optimal' tetrahedral rotation angles of ca. 8°). This is in accordance

with the findings of, e.g., Foster (1960), who postulated an increase of octahedral Al with increasing Fe^{2+} in biotite. Guidotti et al. (1975), studying the crystal-chemistry of natural biotites from northwestern Maine stemming from various metamorphic grades, questioned Foster's results and found no clear correlation between their Al^{VI} content and Mg/Fe ratio. In Fig. 12, we have plotted Al^{VI} , $\text{Al}^{\text{IV}} - 1$ (i.e., Tschermak balanced Al^{VI}), and excess Al^{VI} of 450 biotites from low- to high-grade metamorphic pelitic schists from northwestern Maine (data were provided by D. J. Henry) as a function of their magnesium number X_{Mg} . Considering Al^{VI} (black dots), data cluster at intermediate X_{Mg} and levels of Al^{VI} between ca. 0.35 and 0.55 apfu without a clear mutual dependence in accordance with the findings of Guidotti et al. (1975). If we plot $\text{Al}^{\text{IV}} - 1$ vs. X_{Mg} , a similar picture emerges as found by Benisek et al. (1999, their Fig. 10), i.e., Mg-rich biotites tend to have a lesser degree of Tschermak substitution than more Fe-rich ones (a similar trend was noted for calcic amphiboles by Robinson et al. 1982). This is in agreement with what can be read off from the Al^{VI} isopleths, as shown in Fig. 11a. The predicted range of ~ 0.15 to ~ 0.4 apfu for the Tschermak substitution-balanced octahedral Al content in biotites is in good agreement with that appearing in Fig. 12 (red dots) for the biotites of Maine, which nearly all lie in a band characterized by tetrahedral rotation angles between 7° and 9° (see also Benisek et al. 1999).

Compared to *our calculations*, isopleths from a *W14 calculation* indicate systematically lower Al^{VI} contents in biotite for a given bulk composition and temperature, too low to be consistent with evidence from, e.g., the natural Maine biotites shown in Fig. 12 (red dots), especially at low-grade temperatures, where $\text{Al}^{\text{VI}} < 0.1$ apfu is predicted (Fig. 11b). Toward higher metamorphic grades (temperature), this difference of ca. 0.2 Al^{VI} apfu between *W14* and in *this study* computed Al^{VI} decreases.

A remarkable feature of almost all of the 450 natural biotites from Maine (and probably for metamorphic biotite in general) is the fact that these contain appreciable amounts of excess Al^{VI} , i.e., Al^{VI} in excess to that balanced by the Tschermaks substitution (Fig. 12, blue dots). The data for this excess Al^{VI} cluster around 0.1–0.25 apfu at roughly 1:1 Fe:Mg ratios, and its values seem to increase in Mg-rich bulk compositions. It is obvious from Fig. 12 that biotite activity models should account for this presence of excess Al^{VI} by introducing, e.g., a muscovite- or a K-vacancy component. We will do this in a forthcoming paper that presents a comprehensive biotite activity model extending that of this study to include excess Al^{VI} , Ti, and Fe^{3+} biotite endmembers.

Fig. 8 T - $X_{\text{FeO}/(\text{FeO} + \text{MgO})}$ pseudosection as in Fig. 7, with isopleths of $\ln K_D$ of the Fe–Mg exchange between biotite and garnet, illustrating the bulk composition dependence of $\ln K_D$. Solid isopleths represent *our* calculation, broken lines a *W14* calculation

Pseudosections of natural rocks in the KFMASH system

In this section, we use our KFMASH-biotite model to model two natural rocks, one who has experienced high- T , low- P conditions, and another one that has experienced high- P , low- T conditions. These two rocks have been modeled in the past in the KFMASH system using the predecessors of the *W14* biotite model, i.e., the high- T , low- P rock by Pitra and de Waal (2001) and Tajčmanová et al. (2009) and the high- P , low- T rock by Wei and Powell (2003). These examples, therefore, merely show how the relationships between phases change with *our* model compared to the *W14* biotite model in the KFMASH system. They cannot be used for validation of our biotite model, because the addition of Fe^{3+} , Ti, di-tri-octahedral Al substitutions will modify the results and will increase the number of phases in the mineral assemblage. As mentioned above, this extended chemical system will be explored in a forthcoming paper. Therefore,

the results discussed in this paragraph should be seen as resulting from a model in progress.

Pseudosection of a high- T -low- P metapelite

Pitra and de Waal (2001) (*PdW*) studied phase relations in high- T , low- P metapelites enclosed in granites of the Bushveld Complex using the simplified KFMASH system. They described an early paragenesis with andalusite (chiastolitic) + cordierite + biotite + quartz $\pm$ garnet recording P - T conditions of 550–600 °C and 2 kbar as was calculated by KFMASH pseudosection thermobarometry. This assemblage was transformed into a peak paragenesis containing garnet + sanidine + cordierite + biotite $\pm$ quartz and subsequently into spinel–cordierite symplectites (replacing earlier chiastolitic and) in a 2nd high- T event. This peak event was estimated to have occurred at 750–800 °C, again, based on the interpretation of KFMASH pseudosections in their original study. This heating event is attributed to the emplacement of nearby dry and hot A-type granites.

Fig. 9 Plot of the experimental data of Perchuk and Lavrent'eva (1983, PL83) on the Fe–Mg exchange between biotite and garnet ($P = 6$ kbar): $\ln K_D$ vs. T is shown with error bars of 2σ in **a**, Al^{VI} of biotite (microprobe data from Aranovich et al. 1988) vs. T in **b**. *Perple_X*-computed $\ln K_D$ and Al^{VI} based on *our calculation* are drawn as solid lines and as broken lines resulting from a *W14 calculation* (bulk composition used is given in Table 1)

According to PdW, Al^{VI} in biotite should range between 0.31 and 0.52 in the sanidine + cordierite + biotite + quartz ($\pm$ garnet) stability fields. Tajčmanova et al. (2009) recalculated in their Fig. 2a KFMASH P – T pseudosection for sample X567 of PdW. Because they found that $\text{Al}^{\text{VI}} (= X_{\text{Al}}^{\text{M1}})$ in biotite was too high in these fields compared to that expected, they changed the enthalpy of the Fe–Mg ordering reaction $2/3$ phlogopite + $1/3$ annite = ordered Fe–Mg biotite (Obi, see part-I) to -6.8 kJ/mol to achieve a better agreement with the natural observations. Here, we demonstrate that such a change in the ordering enthalpy, which they had used as a fitting parameter, is not necessary and that the observations are readily explained by either *our* new model or the *W14* model which both use an enthalpy of ordering of -2 kJ/mol.

Performing *our* and *W14 calculations* to sample X567 under water-saturated conditions (bulk given in Table 1) yields the P – T pseudosections shown in Fig. 13a, b. Both are consistent with the petrographic evidence of the first low- T metamorphic event, i.e., show a stability field for the early paragenesis

(andalusite + cordierite + biotite + quartz $\pm$ garnet) followed by biotite + cordierite + sanidine + quartz with rising temperatures. However, in the *W14 calculation*, the wet solidus is already reached before the peak metamorphic assemblages could be established, i.e., garnet + cordierite + biotite + sanidine and finally cordierite + spinel parageneses at the highest T . In contrast, in *our calculation*, biotite breaks down at lower T (blue line in Fig. 13a). As biotite is no longer part of the assemblage, the melting temperature of the remaining mostly ‘dry’ minerals at water-saturated conditions is increased, and melt forms at about 50° higher. Because of this, the garnet + cordierite + biotite + sanidine and finally cordierite + spinel parageneses are established without any melt involvement. This example shows that the choice of biotite model in the KFMASH system can have a large effect on when partial melting would take place.

In the *W14* (and *PdW*) calculation, the peak assemblages are metastable with respect to melt. Large-scale melting would form leucosomes, and these were not observed by PdW. Suprasolidus relationships resulting from the *W14*

Fig. 10 P – T pseudosection in the KFMASH system for an ‘average metapelite’ (Table 1) resulting from **a** our calculation, compared to **b** a W14 calculation (White et al. 2014, their Fig. 4). Subsolidus equilibria are calculated under water-saturated conditions, while suprasolidus equilibria were calculated with a fixed bulk H_2O of 6.65 mol%

Fig. 11 T - $X_{\text{FeO}/(\text{FeO} + \text{MgO})}$ pseudosection in the KFMASH system for the ‘average metapelite’ shown in Fig. 11 under water-saturated conditions. Iso-pleths are Al^{VI} (apfu) in biotite. **a** is based on *our* calculation; **b** on a *W14* calculation

Fig. 12 Plot of octahedral Al of biotite as a function of its $X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Fe})$ content for 450 biotites from low- to high-grade metapelitic samples from northwest Maine. Al^{VI} is the total octahedral Al (black); $\text{Al}^{\text{IV}} - 1$ is the Tschermak substitution-balanced octahedral Al (red), and excess Al^{VI} is the difference between the two (blue, all in apfu). Solid red lines define a band of tetrahedral rotation angles between 7° and 9° , respectively (Benisek et al. 1999). The extent of the Tschermak substitution in natural biotites seems to concentrate in this field. See text for further discussion

calculation using 7 wt% H_2O (the amount that was needed to replicate wet solidus) gives unrealistic estimates between 5 and 10 vol% melt for the garnet–cordierite–biotite–sanidine–melt assemblages (Fig. 13b). Therefore, the *W14* (and *PdW*) calculation requires a lowering of the H_2O activity to get to the right-phase assemblages. Dry conditions were also inferred by *PdW* due to the preservation of contrasting parageneses, by the presence of symplectites (rapid nucleation, slow growth), and by the absence of fibrous sill. To simulate dry conditions, a $\log_{10}(a_{\text{H}_2\text{O}})$ - T pseudosection was constructed (Fig. 13a) at 2.6 kbar (the peak P inferred by *PdW*) using our calculations and at 3.2 kbar using a *W14* calculation. The purple isobaric lines in the pseudosection in Fig. 13b and the one in the $\log_{10}(a_{\text{H}_2\text{O}})$ - T pseudosection below are the same states at their respective pressure and water-saturated conditions with an H_2O activity of 1 ($\log_{10}(1)=0$). As is well known, the lowering of water activity (a) decreases the T of dehydration reactions and (b) increases the T of melting reactions. However, the magnitude of these effects does depend on the details of both biotite solution models as shown by the $\log_{10}(a_{\text{H}_2\text{O}})$ - T pseudosection.

PdW report that biotite in the garnet–cordierite–biotite–sanidine assemblage has $X_{\text{Fe}}^{\text{Bt}} = 0.75\text{--}0.81$, $X_{\text{Fe}}^{\text{Crd}} = 0.64\text{--}0.69$ and $X_{\text{Fe}}^{\text{Grt}} = 0.90\text{--}0.92$. The microprobe analysis of matrix biotite from sample X567 gives $\text{Al}^{\text{VI}} = 0.48$ apfu and $X_{\text{Fe}}^{\text{Bt}} = 0.78$ (*PdW*, Table 2). In both the P - T and $\log_{10}(a_{\text{H}_2\text{O}})$ - T plots of Fig. 13a, the Al^{VI} isopleths of biotite are given. At 2.6 kbar, $T = 667^\circ\text{C}$, and $\log(a_{\text{H}_2\text{O}}) = -0.133$, the computed compositions ($X_{\text{Fe}}^{\text{Bt}} = 0.73$, $\text{Al}^{\text{VI}} = 0.43$ apfu, $X_{\text{Fe}}^{\text{Crd}} = 0.65$, $X_{\text{Fe}}^{\text{Grt}} = 0.92$) come nearest to the observed ones and only $X_{\text{Fe}}^{\text{Bt}}$ and Al^{VI}

are lower by ca. 0.02 and 0.04 mol fractions compared to measured compositions, respectively.

The *W14* calculations show that under lower water activities, the solidus is moved to higher temperatures, and the garnet–cordierite–biotite–sanidine and finally cordierite + spinel parageneses form before melting occurs. For a *W14* calculation, the best agreement with mineral–chemical data for sample X567 is obtained at a higher pressure of 3.2 kbar, $T = 727^\circ\text{C}$, and $\log(a_{\text{H}_2\text{O}}) = -0.1$: $X_{\text{Fe}}^{\text{Bt}} = 0.80$, $\text{Al}^{\text{VI}} = 0.40$ apfu, $X_{\text{Fe}}^{\text{Crd}} = 0.65$, and $X_{\text{Fe}}^{\text{Grt}} = 0.9$.

At this moment, we have no means to say which of the models performs better as we have only worked in the simplified pelitic KFMASH system and tried to apply this to a chemical complex natural system. Validation of either model is not possible. However, the example does clearly show how the biotite model parameters of either model can result in quite different P - T - $a_{\text{H}_2\text{O}}$ pathways the rock could have undertaken. A typical question for many high- T , low- P studies is if dry conditions were reached before (partial) melting takes place, i.e., if water-saturated conditions prevailed, as is often assumed for prograde metamorphism. The earlier breakdown of biotite, which was also demonstrated by the model pelite system in KFMASH from the last paragraph, as shown by this example will influence at which temperature partial melting will start. It shows that biotite influences when dry conditions are reached as no dehydration is expected after the biotite-out curve. This example, therefore, shows that the important role biotite has in solving this question. Our new biotite model predicts, in the KFMASH system, in contrast to the *W14* model, that biotite breaks down at lower temperatures before partial melting starts, which would move the (now dry) solidus to higher temperatures.

It cannot be repeated enough that the results from this paragraph are for the KFMASH system only. The addition of Fe^{3+} , Ti, di-tri-octahedral Al substitutions could potentially modify these results.

Pseudosection for a high-*P* low-*T* metapelite

As an example of *our calculations* on a high-*P*, low-*T* metapelite, we show phase relations for a garnet–phengite–biotite gneiss (sample M4, from the Dabie Shan area, central China), studied by Wei and Powell (2003), *WP03*, their Fig. 10 in Fig. 14a and compare it to an analogous *W14 computation* (Fig. 14b) in the KFMASH system. Both *P*–*T* pseudosections, constructed with the KFMASH bulk

composition, estimated by *WP03* for sample M4 (Table 1) appear almost identical concerning the distribution of stability fields of the mineral assemblages. The biotite-out (blue) line in *our calculation* occurs at about 1–2 kbar lower pressures. With regard to biotite, in KFMASH, isopleths of Al^{VI} show decreasing values with increasing pressure in both types of calculations. The parallelism between the Si content of phengite, a known barometer (Wei and Powell 2003), and biotite's Al^{VI} content in biotite is striking and raises the hypothesis that Al^{VI} is a pressure indicator in KFMASH, especially in low-variance assemblages, such as garnet–chlorite–biotite–phengite–quartz, where it becomes independent of bulk composition, as many of the compositional degrees of freedom are fixed by the mineral assemblage. However,

Fig. 13 *P*–*T* pseudosection in the KFMASH system for high *T*–low *P* (granulite facies) rock X567, studied by Pitra and de Waal (2001), resulting **a** from *our calculation*, compared to **b** a *W14 calculation*. Blue line indicates the final breakdown of biotite, and the red line is the wet solidus. Subsolidus equilibria in the *P*–*T* pseudosection are calculated under water-saturated conditions, while suprasolidus equilibria were calculated with a fixed bulk H_2O of 7.00 mol%. Phase assemblage names in bold indicate the two peak metamorphic assemblages. Below the *P*–*T* pseudosection, a $\log_{10}(a_{\text{H}_2\text{O}})$ –*T* pseudosection

is given. Purple lines in the pseudosections above and below indicate the same thermodynamic states at 2.6 kbar (**a**) and 3.2 kbar (**b**) and water-saturated conditions with an H_2O activity of 1 ($\log_{10}(1)=0$). Going down in the $\log_{10}(a_{\text{H}_2\text{O}})$ –*T* pseudosection shows the phase relationships that would establish if the activity of water was lowered at pressures as indicated by the isobaric purple line. Isopleths are Al^{VI} in biotite (apfu) and are drawn in color in both the *P*–*T* and the $\log_{10}(a_{\text{H}_2\text{O}})$ –*T* pseudosections

before we can make any generalizations and before we start testing the hypothesis that Al^{VI} is a pressure indicator also in more complex chemical systems, we first need to extend *our biotite model* to incorporate Ti, Fe^{3+} , and the di–tri–octahedral substitution.

Conclusions

The application of our new biotite activity model and standard-state thermodynamic properties of Ann, Phl, and Eas presented in part-I to experimental phase equilibria and natural pelitic rocks, using mainly the software *Perple_X*, allows the following conclusions to be drawn:

- Biotite in the experimental Fe–Mg exchange data between biotite and olivine (Zhou 1994) had no or only minimal Al^{VI} , which is confirmed by pseudosection calculations with the experimental bulk composition. To extract, e.g., annites' standard enthalpy of formation value, Zhou's data are superior to existing biotite–orthopyroxene or biotite–garnet exchange data, because the extent of Tschermak substitution in biotite in the latter is not negligible.
- The Fe–Mg distribution between biotite–garnet, biotite–garnet–cordierite, and biotite–orthopyroxene are independent tests of the validity of *our calculations* presented herein. The biotite–orthopyroxene and Fe–Mg exchange equilibria between cordierite, garnet, and biotite are reasonable modeled by either *our* and *W14* biotite models. However, the new biotite a – X relations in combination with the new enthalpy of formation value of biotite end-members, as derived in part-I (Tables 7, 8), unlike the *W14* biotite, successfully reproduce the FS78 experimental data. The resulting $\ln K_D$ values as a function of temperature are in good agreement with the experimental brackets of FS78s bulk composition of $\text{Alm}_{90}\text{Py}_{10}$ experiments (Figs. 3, 7, 8). The alternate biotite models, calibrated with symmetric $W_{\text{PhlAnn}}^{\text{G}}$ and/or models that used $W_{\text{FoFa}}^{\text{G}}$ around 10 kJ/mol (one-site basis) in the thermodynamic analysis of olivine–biotite Fe–Mg exchange data from Zhou (1994) to derive $W_{\text{PhlAnn}}^{\text{G}}$, are not compatible with FS78 experiments.
- *Our calculations* pertinent to the garnet–biotite reaction with more Mg-rich bulk compositions yield less negative $\ln K_D$'s in accordance with experimental evidence [experiments of Gessman et al. (1997), with $\text{Alm}_{80}\text{Py}_{20}$ and $\text{Alm}_{70}\text{Py}_{30}$ as exchange partner of biotite, Fig. 4]. *W14 calculations* show the opposite trend (Fig. 5). The dependence of $\ln K_D$ on bulk- X_{Mg} is shown in a T – X_{Fe} pseudosection, which makes clear that the calibration of FS78 only applies to Fe-rich bulk compositions as used in the experiments and will yield too high temperatures when applied to more Mg-rich bulks far outside the experimental range.
- The predicted Al^{VI} contents for *our* as well as *W14 calculations* in biotite for G97 experimental bulk compositions ranges between ca. 0.3 and 0.45 apfu and are both in good agreement with measured values of G97 (microprobe data). Analogous computations for the somewhat Fe-richer FS78 bulk compositions indicate that also biotite in the FS78 exchange experiments contained Al^{VI} in the same order of ca. 0.3–0.4 apfu. Various speculations and assumptions on the extent of the Tschermak substitution in FS78 biotites (e.g., Holdaway 2000) can now be refuted based on this computational evidence. This is further supported by calculations with a more Mg-rich bulk composition as was used by PL83 in part of their biotite–garnet(–cordierite) Fe–Mg exchange experiments ($X_{\text{Mg}}^{\text{bulk}} = 0.4$). The predicted Al content of biotite is also in accordance with the measured one in this case for both *our* and *W14 calculations* (Fig. 9).
- Low variance fields in KFMASH pseudosection for an average metapelitic rock (Fig. 10) are shifted by ca. 50 K to lower T 's at high- T , low- P conditions and to lower P at higher P conditions as a result of the new biotite activity model and annite standard state properties. The relative increase of low-variance fields over high-variance fields containing biotite shows its increased potential for (pseudosection) thermobarometry, as, in these fields, the exchange relationships between the phases are mainly dependent on P , T and not on the bulk composition.
- As shown for the Maine biotites (Fig. 12), Tschermak substitution-balanced octahedral Al (i.e., $\text{Al}^{\text{IV}} - 1$) in natural biotites increases slightly with increasing $X_{\text{Fe}}^{\text{Bt}}$, a trend already noted by Benisek et al. (1999). This trend and the amount of this 'Tschermak'– Al^{VI} are correctly predicted for an average pelite bulk composition using the new biotite activity model and annite standard state properties (Fig. 11). It seems to be related to the fact that tetrahedral rotation angles between 7° and 9° are energetically favored in the biotite structure.
- The upper thermal stability of biotite is reduced using *our biotite model* in KFMASH. This means that biotite can already break down before the wet solidus is reached. Partial melting would then depend on the dry solidus, which occurs at higher temperatures. It is often assumed that biotite dehydration reactions occur until the wet solidus is reached and, therefore, that water-saturated conditions can be assumed in the prograde path. Our biotite model questions that assumption in the KFMASH system.
- The upper pressure stability of biotite is reduced resulting from *our calculations*. Biotite Al^{VI} shows some potential as a barometer in the KFMASH system, especially in low-variance assemblages.

Fig. 14 P – T pseudosection in the KFMASH system for a high-pressure metapelite (sample M4), studied by Wei and Powell (2003), resulting **a** from *our* calculation, compared to **b** a *W14* calculation. The phase equilibria are calculated assuming water and quartz saturated conditions (i.e., the activity of water and quartz are set to 1). A blue line indicates the breakdown of biotite. The red line is the wet solidus. Black broken lines show the Al^{VI} (apfu) in biotite. Colored lines show the Si-in-phengite (white mica), which has been used as a barometer in earlier studies (e.g., Wei and Powell 2003)

- There is a high need to extend the current model to incorporate Ti, Fe³⁺, and the di–tri-octahedral substitution to see if the relationships that we have found for our natural rocks in the KFMASH system hold in more complex chemical systems.

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