

The b_0 lattice parameter and chemistry of phengites from HP/LT metapelites

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Abstract: The statistical b_0 method is based on the fact that the cumulative b_0 values of white K-micas (WKM) from metapelites of a specific bulk composition can be used, in the lowermost T range of metamorphism, as a semiquantitative P indicator: mean b_0 values (and related celadonite content) in WKM increase with increasing P, thus characterizing the baric type of metamorphism. The solid petrological framework of this method includes specific constraints on rock bulk composition and need of other conditions. In this way, a reference b_0 scale for LT metapelites has become available in the literature, covering the whole range of metamorphic P. However, after many publications based on it, which made a large amount of data available, revision of this b_0 scale is now opportune, and the primary need is a better definition of the reference b_0 values and WKM chemistry for HP/LT metapelites.

Such a better definition is the aim of this paper. The considered HP/LT metapelites come from various terrains: Schistes Lustrés of W Alps, Diablo Range (Franciscan Complex of California), Phyllite-Quartzite Unit of Crete and Peloponnese, UHP gneiss from Dora Maira, Attic-Cycladic Complex of Sifnos, Tavsanli Zone and Nilüfer area of NW Turkey. In addition, WKM chemical and b_0 data were used from various sources.

The new chemical and b_0 data (EMPA and XRPD) allowed us: (i) to establish the reference b_0 and chemistry of WKM from HP/LT metapelites: b_0 turns out to be around 9.040 Å; (ii) to confirm and extend to HP/LT metapelites the petrological basis of the b_0 method, particularly the control of mineral assemblages on b_0 values; (iii) to glimpse more complex relationships between b_0 and Si than those currently known, and particularly the importance of the $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ ratio; (iv) to ascertain the validity of the b_0 method for detecting generic HP/LT conditions; (v) to ascertain the inability of the b_0 method to discriminate, within the above HP field, differences between various P/T regimes, mainly due to still poorly known crystal-chemical problems, and the fact that comparative b_0 interpretations of various HP/LT sample populations from different belts are impeded by poor understanding of the extent of re-equilibration of WKM at higher T and lower P during exhumation.

Key-words: phengite, XRPD, b_0 parameter, EMPA chemistry, HP/LT metapelites, semiquantitative geobarometry.

1. Introduction

Starting from results by Sassi (1972), Sassi & Scolari (1974) found that the cumulative b_0 values of white K-micas in low-grade metapelites of a specific bulk composition could be used as metamorphic P indicators for the lowermost T range of metamorphism: b_0 values increasing with increasing P, thus characterizing the baric type of metamorphism. Guidotti & Sassi (1976) showed that b_0 is essentially a function of celadonite content (see also Guidotti *et al.*, 1989, 1992), and specified the constraints of the rock bulk composition – as expressed by the mineral assemblage in an AKNa projection (*ibid.*, Fig. 11) – and the need for other compositional constraints (*e.g.*, occurrence of a phase buffering f_{O_2}) for the correct use of b_0 as a semi-quantitative geobarometer in metapelites. Padan *et al.* (1982) extended the use of the method to anchimetamorphic pelites. The firm petrological

grounds of this method were restated by Guidotti & Sassi (1998a, p. 837), together with the possible sources of misuse.

Although the use of the b_0 cell parameter as a semiquantitative geobarometer has been criticized, for instance, by Essene (1989), it has been successfully applied in many areas throughout the world, **both before** Essene's warning (*e.g.*, Altherr *et al.*, 1979; Árkai *et al.*, 1981; Bossière *et al.*, 1979; Briand, 1980; Brill, 1988; Brime, 1985; Diaz de Federico *et al.*, 1979; Fettes *et al.*, 1976; Franceschelli *et al.*, 1989; Frey *et al.*, 1983; Gomez-Pugnaire *et al.*, 1977; Iwasaki *et al.*, 1978; Kräutner *et al.*, 1976; Offler & Prendergast, 1985; Offler *et al.*, 1987; and references quoted therein), **and after it** (*e.g.*, Árkai, 1990; Árkai *et al.*, 2002, 2003 a, b; Brime *et al.*, 2003; Nishimura *et al.*, 2000; Offler & Brime, 1994; Offler *et al.*, 1998a,b; Wang *et al.*, 1996). Wang *et al.* (1996, p. 109) consider that “the statement by Essene (1989) that ‘it

seems prudent to avoid the use of Sassi's phengite barometer for thermobarometry' seems not justified".

Although Sassi's method is not a sophisticated but rather a "poor man's" procedure of a statistical nature, its use has three particular advantages: *a*) it involves a *quick, simple, and low-cost* analytical procedure; *b*) it is applicable to rocks for which low to very low T and rock bulk composition preclude the appearance of P-indicator mineral phases and low variance mineral assemblages; *c*) so far, it is the only reliable, easy-to-use barometric indicator applicable to rocks in which low to very low T and the common occurrence of an intergranular carbonaceous film impose so fine a grain-size on the mica flakes that the possibility of obtaining reliable EMPA becomes remote. In conclusion, the b_0 geobarometer *is the only method which is easily and inexpensively applicable to anchi- and epimetamorphic pelitic terrains on a regional scale.*

We are aware that low-grade and very low-grade rocks are also studied using other approaches, some closely linked to thermodynamic parameters and reasoning, and also giving reliable geobarometric results (*e.g.* Rimmele *et al.*, 2005, and references therein), and others highly dependent on advanced sophisticated technologies (*e.g.* Li *et al.*, 1994 a, b; Nieto *et al.*, 2005); phengite crystals can be studied even at the nanoscale for geobarometric purposes (*e.g.* Ferraris *et al.*, 2005). We appreciate these approaches, but also believe that easy-to-use methods, when based on solid petrological grounds and when rigorously used, are also useful and reliable scientific tools for the advancement of knowledge in Geology.

However, a revision of Sassi & Scolari's (1974) b_0 scale is now opportune, and the primary need is a better definition of the reference b_0 values and mica chemistry for HP/LT metapelites, because they were poorly defined (see below).

Such a better definition is the only aim of the present paper. Neither a proposal of a quantitative geobarometer for the considered T-P range, nor the study of specific crystallochemical relations (which are only discussed occasionally) fall within the scope of this paper.

The mineral abbreviations used in the present paper are those proposed by Kretz (1983). In addition: Phe = phengite(s); WKM = white K-mica(s).

Earlier b_0 values on phengites from high P/T terrains. The samples used by Sassi & Scolari (1974) for the high-P range terrains (Daday-Ballidag and Sanbagawa), with mean b_0 values of respectively 9.056 and 9.054 Å, do not have the appropriate pelitic composition, but are mainly metabasites. Moreover, the Sanbagawa belt only represents a transitional intermediate-high P/T rather than a high P/T metamorphic gradient (*e.g.*, Yardley, 1989, pp. 102–103; Miyashiro, 1994, p. 200).

Iwasaki *et al.* (1978) therefore measured new b_0 values on the Sanbagawa metapelites, and found a mean b_0 value of 9.032 Å for 36 samples from the upper Chl zone (Pmp-Act zone in metabasites). Assuming a subsequent higher-temperature, Barrovian-type overprint, these authors concluded that the representative b_0 values for the Sanbagawa glaucophanitic greenschist-facies metapelites should be higher than the 9.032 Å found, but lower than 9.054 Å, the value obtained from the Sanbagawa metabasites by Sassi & Scolari (1974).

Since the paper of Iwasaki *et al.* (1978), numerous chemical data have become available on the WKM of several well-studied HP/LT terrains, including the Schistes Lustrés of the Alps (Agard *et al.*, 2001), the Diablo Range in the Franciscan Complex of California (Dalla Torre *et al.*, 1996a, b), the Phyllite-Quartzite Unit of central and western Crete and the Peloponnese (Theye, 1988; Theye *et al.*, 1992; Jolivet *et al.*, 1996), a few on the Tavsanli Zone of NW Turkey (Okay, 2002) and on the Attic-Cycladic complex on Sifnos (Okrusch *et al.*, 1978; Trotet *et al.*, 2001a, b), with additional b_0 data without chemical analyses (Altherr *et al.*, 1979). These chemical data are now supplemented with the missing b_0 data (or *vice versa*) from the same metapelites, in order to document and constrain the range of b_0 values for HP/LT metapelites. In addition, for the present research, a suite of samples was collected from the Tavsanli Zone in NW Turkey, which appear to represent unusually high P/T gradients (Okay, 2002).

Not considered in this paper are other studies on the b_0 distribution from transitional medium/high-P terrains and retrograded blueschists (*e.g.*, Árkai & Kovacs, 1986; Árkai *et al.*, 2003a). The results of these papers have not been included here, in order to focus more attention on the areas listed in the above paragraph.

One last aspect to be considered is the polytypism of HP/LT WKM. Metamorphic WKM are well-known to be commonly $2M_1$, but they are $3T$ in HP/LT rocks (Sassi *et al.*, 1994, and references therein). Therefore, in principle this problem may be relevant to the present study, which only deals with HP/LT rocks. However, as regards the aspects dealt with here, this problem can be disregarded: we recall that 060,331 diffractions of $2M_1$ become 030 and 300 respectively in $3T$ stacking, thus coinciding exactly (Rieder *et al.*, 1992).

2. Data-base and outlines of metamorphic conditions in the considered areas

2.1 Data-base

Concerning both b_0 values and chemistry of Phe, the data-base used consists of four types of data, some taken from the literature, some obtained from the respective authors, and some new data (both EMPA and/or b_0), specifically carried out for the present research. Material was requested from authors or collected in the field from the following HP/LT metamorphic areas.

(i) Samples with published chemical analyses of phengites without b_0 data from:

- the Schistes Lustrés complex of the W Alps (Agard *et al.*, 2001),
- the Diablo Range in the Franciscan Complex of California (Dalla Torre *et al.*, 1996a, b),
- the Phyllite-Quartzite Unit of Crete and the Peloponnese (Theye, 1988),
- the UHP gneiss from the Dora Maira (Schertl *et al.*, 1991).

(ii) Samples with published b_0 determinations without chemical analyses from:

- the Attic-Cycladic complex on Sifnos (Altherr *et al.*, 1979); a few Phe were analysed by Okrusch *et al.* (1978, Table 3).
- (iii) *Samples without either b₀ data or chemical analyses in the literature, collected in the field by one of the coauthors (H. J. K.) from:*
 - the Tavsanlı Zone and Nilüfer area (Karakaya Zone) of north-west Turkey (Okay, 2002).
- (iv) *In addition, analysed phengites with b₀ data were used from various sources, including Ernst (1963), Fiorentini Potenza (1969), Cipriani *et al.* (1968), Schwander *et al.* (1968), Frey *et al.* (1983) and Schertl *et al.* (1991).*

All chemical and b₀ data used for this paper are listed in a large Data-base not included in the paper, but deposited at the EJM editorial office.

2.2 Notes on the considered HP/LT areas, with special reference to metamorphic geotherms and the possible formation or re-equilibration of phengites during HT overprints upon uplift

*Schistes Lustrés complex, Franco-Italian W Alps (Agard *et al.*, 2001)*

Metapelites metamorphosed at conditions varying from 350°C, 8–12 kbar to 450–500°C, 18–20 kbar. The T of the Crp = Qtz + Cld + water reaction, marking the Crp/Cld isograd separating the higher-grade eastern Cld zone from the lower-grade western Crp zone, is estimated at *ca.* 350–400°C. Most of the crystallisation and/or re-equilibration of Phe took place during the widespread overprinting of blueschist- or eclogites-facies minerals by greenschist-facies minerals during deformation phases D2 and D3, dated at 45 ± 3 and 39 ± 2 Ma respectively, upon exhumation. The “C1” Phe coexisting with Cld in the Cld zone and the few ‘A’ Phe cogenetic with Car are notably more celadonic than the “C2” Phe associated with Chl replacing Cld and the “B1” and “B2” overgrowing Phe.

*Diablo Range, Franciscan Complex, California (Dalla Torre *et al.*, 1996a, b)*

The Franciscan Complex was metamorphosed at 100–155 Ma. Peak P assemblages in the Diablo Range include jadeitic Px, sodic Amph, Lws, Arg and Phe, and represent P of 7–9 kbar and T of 200–250°C at Mount Hamilton and 8–10 kbar and 250–300°C at Pacheco Pass (Dalla Torre *et al.*, 1996a, Table 1). The transition of Arg to Cal, formation of Ab from jadeitic Px + Qtz, compositional gradient from Phe to Ms (see also Dalla Torre *et al.*, 1996b) and transition from sodic to calcic amphibole indicate a lower-P, possibly higher-T overprint from blueschist- to greenschist-facies conditions, considered to have taken place at 5–8 kbar and 300–350°C with a geothermal gradient of ≈14°C/km. The WKM in some of the samples cover a compositional range as broad as 3.1–3.9 Si apfu and 0.2–1.0 Mg+Fe apfu (Dalla Torre *et al.*, 1996b, Fig. 4), and the b₀ measurements therefore represent a physical mixture of numerous small Phe domains and smaller numbers of muscovitic domains.

*Phyllite-Quartzite Unit, Crete and the Peloponnese (Theye, 1988; Theye & Seidel, 1991; see also Theye *et al.*, 1992; Jolivet *et al.*, 1996)*

The predominantly pelitic Phyllite-Quartzite Unit of Crete and the Peloponnese underwent HP/LT metamorphism at 24–19 Ma. The grade of the HP/LT metamorphism increases from E to W, as evident from the successive disappearance of the assemblage Prl + Chl and of sudoite (occurring only in E Crete), the appearance of Cld and, in a few cases, Fe-Mg-Car in central Crete, Mg-Car and Law in W Crete, and Alm-rich Grt in the Peloponnese (Theye & Seidel, 1991; Theye *et al.*, 1992). The locally intercalated intermediate metavolcanics contain Pmp, Law, Mg-Rbk/crossite and Agt in E Crete, but no Gln or Jd, which appear only in W Crete. Metamorphic conditions, estimated by Theye & Seidel (1991) and Theye *et al.* (1992) are as follows:

eastern Crete ≈ 300°C, 8 kbar

central Crete ≈ 350°C, 9 kbar

western Crete ≈ 400 ± 50°C, 10 ± 3 kbar

Peloponnese ≈ 450 ± 30°C, 17 ± 3 kbar.

For Crete, this corresponds to a metamorphic geotherm of ≈ 12°C/km.

Thomson *et al.* (1998, 1999) have shown that residence times at HP/LT conditions in W Crete were brief: peak metamorphic conditions for the Phyllite-Quartzite Unit of Central and W Crete were attained between ~24 and 19 Ma, probably only at 21–19 Ma; rapid exhumation from ~35 km to <10 km and <300°C at a rate of >4 km/Ma was completed before ~19 Ma (zircon fission track ages) and, at the latest, 17 Ma.

*Attic-Cycladic Complex on Sifnos, Cyclades (Altherr *et al.*, 1979; see also Trotet *et al.*, 2001a, b)*

The blueschists and related eclogites of Sifnos are from the lower tectonic unit. The assemblage Jd-Gln-Grt is represented, and Okrusch *et al.* (1978) estimated that T's of 450°C were reached at P's of at least 14 kbar, corresponding to an average geothermal gradient of *ca.* 10°C/km. Massonne (1995a, p. 77) calculated a geotherm as low as 5°C/km for the HP event on Sifnos. The assemblage Jd+Qtz is frequently preserved in northern but rarely in southern Sifnos. Phengites from the best preserved metamorphic HP/LT rocks from northern Sifnos give K-Ar and Rb-Sr ages around 42 Ma; those from the less preserved assemblages K-Ar ages between 48 and 41 Ma – ascribed to excess argon – but generally lower Rb-Sr ages (Altherr *et al.*, 1979). The K-Ar and Rb-Sr ages of 24–21 Ma from Phe from central Sifnos date a second, greenschist-facies metamorphic overprint.

Tavsanlı area, NW Turkey (Okay, 2002)

The Tavsanlı zone around Orhaneli, S of Bursa in NW Turkey, represents the subducted N-facing passive continental margin of the Anatolide-Tauride block. It constitutes a coherent metamorphic complex with sodic metapelites (“grey-schists”) containing a low-variance assemblage with Jd + Gln + Cld + Law; associated metabasites contain Na-Amph + Law ± Grt. The stable coexistence of Cld and Jd indi-

cates P of 24 ± 3 kbar and T of $430 \pm 30^\circ\text{C}$ for the peak blueschist metamorphism, corresponding to geotherms as low as $5^\circ\text{C}/\text{km}$ for the Upper Cretaceous blueschist metamorphism (one of the lowest geotherms recorded in high-P rocks). T in the blueschists is not considered to have increased during exhumation.

Nilüfer Formation of Karakaya Complex, NW Turkey (Okay, 2004)

The Nilüfer Formation is a semi-coherent Permo-Triassic metabasic-marble-phyllite series with carbonate and shale bands. It constitutes the lower unit of the Karakaya Complex, the Triassic subduction-accretion units in the Sakarya Zone, a 1500-km long continental fragment between the Anatolide-Tauride block in the south and the Istanbul and Rhodope-Strandja zones and the eastern Black Sea in the north. The Nilüfer Formation underwent HP/LT greenschist-facies metamorphism of latest Triassic age with the development of Ab+Chl+Ep+Act+Ttn in mafic tuffs; Na-Amph occurs very rarely in iron-rich tuffs. The overlying greywacke-shale sequence (Orhanlar Greywacke) is not believed to be affected by the HP/LT metamorphism.

3. Analytical procedures and criteria for evaluating the quality of the chemical data taken from the literature

Measurements of b_0

These measurements were performed on a Philips PW3710 diffractometer, using conventional Bragg-Brentano parafocusing geometry, at the Department of Mineralogy and Petrology of the University of Padova, partly on rock slices cut perpendicularly to the foliation, and partly on disoriented powder prepares, in such a way that the 060 peak is enhanced and not disturbed by other peaks falling in the same 2θ range. In both cases, quartz of the rock and metallic silicon were used as standards. In the rock slides, metallic silicon was included by filling in grooves made with a dentist's drill. The analytical conditions were: 40 kV and 30mA; 54–64 2θ range; step scan mode with step width increments of 0.02 2θ , and step counting time of 2 seconds. Analytical error is ± 0.0006 . As regards the possible occurrence of several WKM generations in a given rock, recalling the statistical nature of the method used, the sharpness of the XRD peaks (when not stated otherwise) indicates that one WKM generation largely prevails over possible others, and that its petrological significance also prevails. The low values of the standard deviation for the b_0 in each considered sample population of our primary interest (X' and Y' types: see below) indicates that the statistical weight of other WKM generations is small and their petrogenetic significance minor.

Use of the composite peak to calculate b_0

Rieder *et al.* (1992) pointed out that what Sassi (1972) and Sassi & Scolari (1974) considered as b_0 was not rigorously based on d_{060} but on the composite peak $d_{060,33T}$. However, they concluded that the technique used is such that the 060 peak is enhanced and decisively prevails, so that its validity

as the basis for calculation of the b_0 lattice parameter is justified. Wang *et al.* (1996) compared b_0 values determined through measurement of the composite peak $d_{060,33T}$ with b_0 values obtained through unit-cell refinement, and showed that the two data sets have a good linear correlation (*ibid.*, Fig. 12), b_0 values from the composite peak $d_{060,33T}$ being only slightly smaller than those from unit-cell refinement, demonstrating the reliability of the simple technique first proposed by Sassi (1972).

Microprobe analyses

These analyses were carried out using a Cameca Camebax electron microprobe of the Institute of Geosciences and Georesources of the CNR at the Department of Mineralogy and Petrology of the University of Padova. The operating conditions were: electron beam current 10 nA; accelerating voltage 15 kv; acquisition time 10 sec for each element and 5 sec on background; beam radius 1 μm . Natural and synthetic standards were used, and the PAP correction procedure was followed. Measurements are affected by a relative uncertainty of 1 % for major (> 5 wt %) and 4 % for minor elements (< 5 wt %).

Quality of chemical data and criteria for rejection of unreliable phengite analyses taken from the literature

Both Fm (=Fe + Mg + Mn apfu) and Si apfu – 6 were used as measures for the “celadonite” content of WKM. In dioctahedral micas, unless there is appreciable substitution of Fe^{3+} for ^{VI}Al , Fm and Si – 6 should be equivalent. The chemical analyses taken from the literature were carried out by various methods. In many of the Phe analyses, particularly older analyses made on mica concentrates by classical (“wet”) analysis, Si is too low and/or Fm is too high: Fm is somewhat higher than Si apfu – 6 in several of the Phe analyses, possibly reflecting Fe^{3+} , but in some extreme cases Mg apfu alone is larger than Si apfu – 6, and/or Si apfu is less than 6 (Fig. 1). Either of these anomalies are likely to reflect the presence of Chl in the analysed concentrates.

Consequently, all analyses with: (1) Mg apfu materially larger than Si apfu – 6, and/or (2) Si apfu less than 6, were rejected as unreliable. This includes 5 out of 7 mica analyses from Ernst (1963) and all the high-Fm mica analyses from Schwander *et al.* (1968).

4. Results

4.1 b_0 ranges of phengites from metapelites of HP/LT areas

The b_0 values measured on the Phe from these terrains are represented by statistic parameters in Table 1 and graphically on the cumulative plots in Fig. 2. In both cases, data are shown separately according to geological provenance and the mineral assemblages explained in section 4.3. At first glance, b_0 seems to vary widely, but after petrological evaluation of each sample group (see below section 4.3), it becomes clear that the reference mean b_0 values for the HP/LT metapelites are in the range 9.038 – 9.042 Å

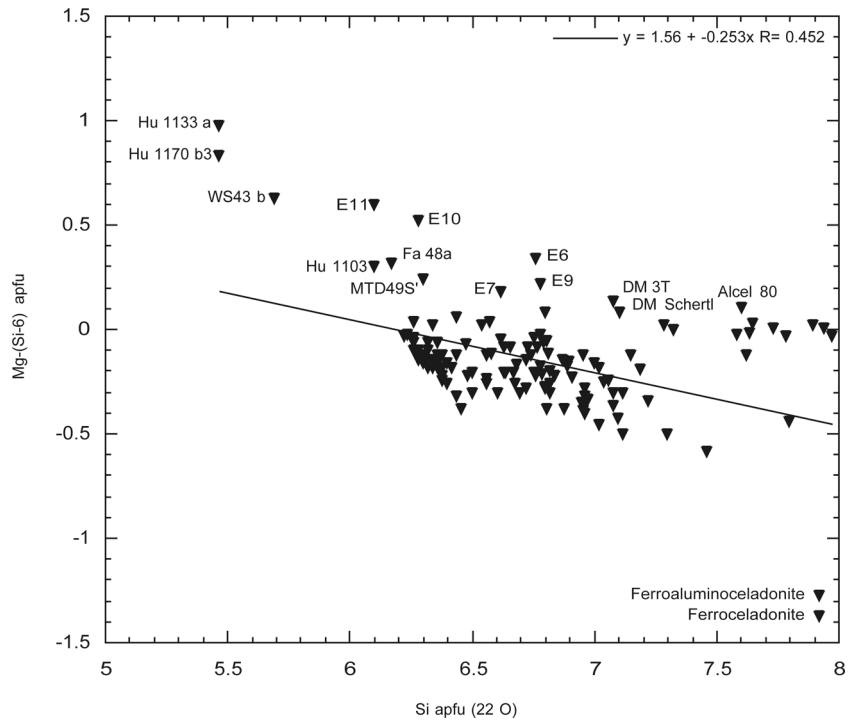


Fig. 1. Mg apfu – (Si – 6) apfu difference plotted against Si content for all phengite analyses in data-base. Analyses with Mg apfu >> (Si – 6) apfu or Si apfu < 0 were probably contaminated by chlorite and were discarded as unreliable. Localization of ferroaluminoceladonite and ferroceladonite are also shown in the plot.

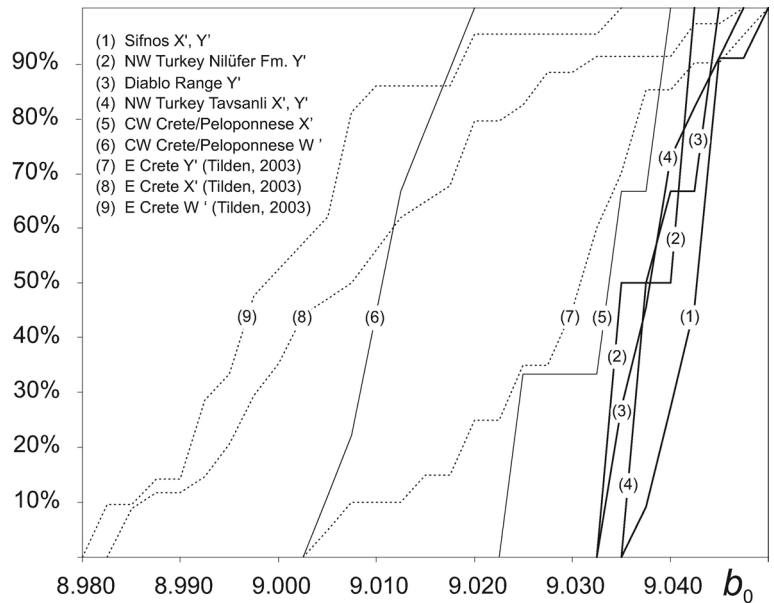


Fig. 2. Cumulative frequency curves of b_0 for phengites of the considered HP/LT metapelites, classified according to geological provenance and mineral assemblage. Each curve is labelled with same number as in Table 1. All b_0 values were measured in Padova, except those of curves 1 (from Altherr *et al.*, 1979) and 7 to 9 (from Tilden, 2003). Wide spread of curves 7 to 9 is considered to reflect incomplete re-equilibration of b_0 at this very low grade of metamorphism. X', Y', W' assemblages: see explanation in section 4.3.

(sample populations and curves #1 to 4 in Table 1 and Fig. 2), and that the lower mean values (#5 and 6) depend on the mineral assemblages, as will be explained below in the mentioned specific section.

The above-defined reference b_0 range is quite similar to the b_0 value ($9.032 < b_0 < 9.054 \text{ \AA}$) estimated by Iwasaki *et al.* (1979) for the Sanbagawa metamorphism, which is related to a metamorphic P/T gradient lower than those of the Sifnos, Diablo Range, Crete-Peloponnese and Tavsanlı areas. Therefore, the question arises: why do the b_0 values not continue to increase at these higher metamorphic P/T gradi-

ents? A number of explanations (including those concerning #7 to 9) are discussed in section 5.

4.2 Chemical results

The analyses of some representative Phe carried out in Padova are listed in Table 2. These results, together with all the analyses from our whole chemical data-base, were used in the various plots and discussions below. Formulas were calculated on the basis of 22 oxygens. However, formulas

Table 1. b_0 values for studied HP/LT phengites, classified according to geological provenance and mineral assemblage. Each line is labelled with numbers 1 to 9 as in Fig. 2. b_0 values were all measured in Padova, except those of lines 1 (from Altherr *et al.*, 1979) and 7 to 9 (from Tilden, 2003). Assemblages X', Y', W' are explained in section 4.3.

HP/LT terrain	Number of samples	Mineral assemblage	Mean value (Å)	σ	Min. (Å)	Max. (Å)
1 Sifnos (Greece)	11	X', Y'	9.042	0.0035	9.0372	9.0498
2 NW Turkey, Nilüfer Fm.	2	Y'	9.039	0.0038	9.0360	9.0414
3 Franciscan Diablo Range (USA)	6	Y'	9.038	0.0049	9.0330	9.0450
4 NW Turkey, Tavsanlı area	11	X', Y'	9.038	0.0038	9.0336	9.0456
5 Phyllite-Quartzite Unit of Kythira (central and western Crete) and Peloponnese	3	X'	9.032	0.0068	9.0246	9.0378
6 Phyllite-Quartzite Unit of central and western Crete and Peloponnese	9	W'	9.011	0.0045	9.0048	9.0187
7 E-Crete, Phyllite-Quartzite unit (data from Tilden, 2003)	20	Y'	9.029	0.0119	9.0040	9.0493
8 E-Crete, Phyllite-Quartzite unit (data from Tilden, 2003)	34	X'	9.009	0.0168	8.9835	9.0454
9 E-Crete, Phyllite-Quartzite unit (data from Tilden, 2003)	21	W'	9.000	0.0126	8.9820	9.0330

on 11 oxygens are only used in the text below, in order to facilitate comparisons with the data and diagrams by Tischendorf *et al.* (2004), with special reference to Fig. 3 b, c.

Of the main isomorphous substitutions affecting WKM (for reviews, see Guidotti & Sassi, 1998 a,b; Parra *et al.*, 2002), the micas we considered record effects of most of them but, as shown below, celadonite substitution turns out to be the most significant.

Some deficiency in the XII site is a common feature, but it is confined within a relatively small range, around a mean value of 0.091 apfu ($\sigma = 0.044$). This deficiency may reflect several variables (see Guidotti & Sassi, 1998 b, p. 62–64; Agard *et al.*, 2001, p. 486–487), including the so-called “pyrophyllite substitution”. The low accuracy of K determination by EMPA should also be recalled. Several authors have interpreted the total amount of deficiency in the XII site as a

measure of the extent of pyrophyllite substitution (*e.g.* Parra *et al.*, 2002; Rimmelé *et al.*, 2005). For our micas, the positive correlation between the deficiency in the XII site vs. Si apfu is very poorly defined, like the negative one vs. Fe+Mg. With these premises, and considering the lack in our case of direct analytical data concerning the real occupancy of the XII site (*e.g.*, NH_4 , *etc.*), caution is necessary when considering such an interpretation.

The extent of paragonite substitution is not significant: X_{Na} ranges around a mean value of 0.053 ($\sigma = 0.037$). Di-tri-octahedral substitution has no petrogenetic significance, since $\Sigma \text{VI}R$ does not significantly exceed 2 apfu of the ideal Ms. As regards Fe^{3+} , we have no data; hence, we can only assume that, as in most metamorphic Ms, a not minimal part of Fe is Fe^{3+} (Guidotti & Sassi, 1998a, b).

The FeMg_{-1} substitution is very important, Fe/Mg ratio ranging from 0.009 to 2.0, with a mean value of 0.764 ($\sigma = 0.408$).

Fig. 3a shows that the data-points clearly define a trend towards celadonite, making a high angle with the arrow indicating Prl substitution. Deviation of the data-point cluster from the Ms-celadonite tie-line reflects the above mentioned deficiency in the XII site. The importance, in our WKM, of celadonite substitution is also clearly shown in Fig. 3b and 3c (from Tischendorf *et al.*, 2004). In plot 3b, we also show the line $\text{VI}R < 2.25$, which may be considered as reference area for dioctahedral WKM (from Tischendorf *et al.* (2004, Fig. 3).

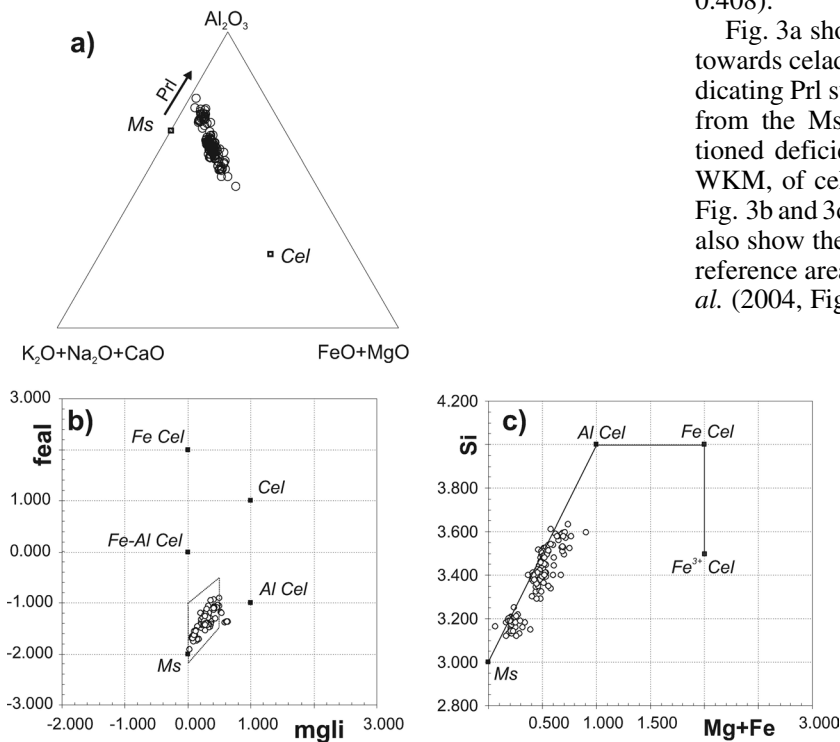


Fig. 3. Main chemical features of studied WKM. Plots 3b and 3c are after Tischendorf *et al.* (2004). Quadrangle in plot 3b is based on line $\text{VI}R < 2.25$ after Tischendorf *et al.* (op. cit., Fig. 3): it may be considered as a reference field for dioctahedral micas. $\text{mgli} = (\text{Mg} - \text{Li})$; $\text{feal} = (\text{Fe}_{\text{tot}} + \text{Mn} + \text{Ti} - \text{VIAl})$.

Table 2. Phengite EMP analyses carried out in Padova for the present paper, and respective b_0 values. They are part of a larger data-base which is deposited at the EJM editorial office.

assembl. sample no.	Western Turkey										Sifnos										Dora Maira
	Nitiifer Fm.					Tavsanli					Northern Sifnos					Central Sifnos					
	wt1A (3)	Y wt1B (6)	Y wt4-2 (4)	X wt10 (4)	X wt11 (2)	Y wt12 (4)	Y wt13B-7 (4)	Y wt14 (3)	Y wt20-4 (4)	Y S174-127 (4)	Y S174-129 (4)	X S174-131 (3)	Y S174-133-5 (4)	X S174-134 (5)	Y S176-290 (4)	Y Si-77-560 (4)	Y S176-156 (3)	Y S176-507p (2)	Y S176-507 (4)	wsch (4)	
SiO ₂	48.97	48.01	50.66	51.44	52.01	51.48	50.24	51.25	51.17	50.82	50.43	49.40	50.62	50.58	50.12	51.05	50.54	49.14	49.52	54.21	
TiO ₂	0.16	0.12	0.20	0.08	0.08	0.16	0.03	0.11	0.23	0.17	0.19	0.21	0.21	0.25	0.22	0.24	0.07	0.18	0.15	0.35	
Al ₂ O ₃	26.92	28.14	27.56	25.79	25.68	24.61	27.72	25.73	25.84	25.28	26.11	26.65	25.75	26.99	26.95	27.36	27.80	28.08	26.45	23.55	
Cr ₂ O ₃	0.04	0.04	0.07	0.06	0.05	0.03	0.02	0.03	0.00	0.03	0.05	0.03	0.01	0.02	0.11	0.01	0.07	0.00	0.02	0.02	
FeO	3.54	4.14	3.33	3.44	3.32	4.51	3.49	3.63	3.12	3.86	2.21	3.18	2.26	2.60	1.80	2.03	2.33	4.08	3.98	0.12	
MnO	0.05	0.02	0.10	0.02	0.03	0.06	0.00	0.06	0.02	0.01	0.01	0.04	0.02	0.00	0.00	0.00	0.05	0.05	0.05	0.00	
MgO	2.69	2.10	2.72	3.00	3.22	2.76	2.12	2.81	3.59	3.36	3.59	2.80	3.69	3.11	3.63	3.52	3.04	2.32	2.59	6.29	
CaO	0.02	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.12	0.01	0.03	0.01	0.00	0.00	0.03	0.03	0.07	0.03	0.01	0.01	
Na ₂ O	0.23	0.32	0.25	0.13	0.17	0.10	0.24	0.11	0.42	0.36	0.45	0.44	0.39	0.61	0.64	0.58	0.40	0.30	0.24	0.15	
K ₂ O	9.96	9.84	10.41	10.46	10.42	10.35	10.25	10.29	10.06	10.38	10.13	10.30	10.24	10.14	9.96	10.02	10.42	10.46	10.48	10.59	
Total	92.58	92.75	95.30	94.44	94.99	94.06	94.13	94.02	94.56	94.29	93.19	93.05	93.18	94.30	93.46	94.85	94.78	94.64	93.49	95.29	
Si	6.758	6.634	6.787	6.949	6.976	7.018	6.805	6.954	6.894	6.908	6.870	6.787	6.900	6.820	6.795	6.816	6.778	6.670	6.800	7.141	
^{IV} Al	1.242	1.366	1.213	1.051	1.024	0.982	1.195	1.046	1.106	1.092	1.130	1.213	1.100	1.180	1.205	1.184	1.222	1.330	1.200	0.859	
^{VI} Al	3.136	3.217	3.138	3.055	3.036	2.971	3.231	3.068	2.997	2.958	3.062	3.102	3.037	3.110	3.102	3.121	3.172	3.161	3.081	2.799	
^{VI} Ti	0.016	0.013	0.020	0.008	0.008	0.017	0.003	0.012	0.023	0.018	0.019	0.022	0.022	0.025	0.022	0.024	0.007	0.018	0.015	0.034	
Cr	0.004	0.005	0.007	0.006	0.005	0.003	0.002	0.003	0.000	0.004	0.005	0.003	0.001	0.002	0.012	0.001	0.008	0.000	0.002	0.002	
Fe ²⁺	0.409	0.478	0.373	0.388	0.373	0.514	0.396	0.412	0.352	0.439	0.251	0.365	0.257	0.293	0.204	0.227	0.261	0.463	0.457	0.014	
Mn ²⁺	0.005	0.002	0.012	0.002	0.003	0.007	0.000	0.007	0.002	0.001	0.001	0.005	0.002	0.000	0.000	0.000	0.005	0.006	0.006	0.000	
Mg	0.554	0.432	0.544	0.604	0.643	0.560	0.429	0.567	0.722	0.681	0.728	0.573	0.750	0.626	0.734	0.700	0.607	0.469	0.531	1.235	
O site	4.125	4.147	4.093	4.064	4.068	4.073	4.061	4.070	4.095	4.100	4.068	4.069	4.069	4.056	4.074	4.073	4.061	4.116	4.092	4.083	
Ca	0.002	0.002	0.000	0.004	0.000	0.000	0.000	0.000	0.018	0.001	0.004	0.001	0.000	0.000	0.004	0.005	0.010	0.004	0.001	0.002	
Na	0.062	0.087	0.064	0.035	0.045	0.027	0.063	0.030	0.109	0.094	0.118	0.118	0.102	0.160	0.167	0.151	0.103	0.079	0.065	0.039	
K	1.754	1.734	1.779	1.803	1.784	1.800	1.772	1.782	1.729	1.800	1.761	1.806	1.780	1.744	1.722	1.707	1.783	1.812	1.837	1.780	
A site	1.818	1.823	1.842	1.842	1.829	1.827	1.835	1.812	1.856	1.895	1.883	1.925	1.882	1.905	1.893	1.864	1.896	1.895	1.902	1.821	
X _{Na}	0.034	0.048	0.035	0.019	0.024	0.015	0.034	0.016	0.059	0.050	0.063	0.061	0.054	0.084	0.088	0.081	0.054	0.042	0.034	0.022	
Fe/Mg	0.737	1.107	0.686	0.643	0.580	0.918	0.923	0.726	0.487	0.645	0.345	0.637	0.343	0.468	0.278	0.324	0.431	0.986	0.860	0.011	
b_0	9.0414	9.0360	9.0210	9.0366	9.0336	9.0426	9.0336	9.0378	9.0414	9.0498	9.0420	9.0426	9.0378	9.0396	9.0408	9.0372	9.0440	9.0426	9.0426	9.0360	

4.3 Control of metamorphic mineral assemblages on b_0 and chemistry of WKM

Guidotti & Sassi (1976, fig. 11, confirmed in 1986, 1998a and 2002), documented systematic differences between the b_0 values (and celadonite content) of WKM in aluminous assemblages, distinguishing four categories of mineral assemblages with different aluminum saturation (and sodium contents), as shown on an AKNa projection:

W assemblage, with Prl + Pg,

X assemblage, with Pg and Ab, but without Prl,

Y assemblage, with Ab, but without Pg, and

Z assemblage, with Ab and Kfs.

At any given P-T value, the WKM celadonite content and b_0 values increase from W to Z. The b_0 scale of Sassi & Scolarì (1974) is related to the bulk composition of assemblage Y, very close to X.

Since many of the rocks studied here contain Cld, Crp, Jd and Gln, and lack Prl and Pg, this classification has been broadened here to accommodate the occurrence of these minerals, exploiting the fact that Chl and Qtz are possible additional phases in all these assemblages. Since Cld and Crp + Qtz are chemically equivalent to Prl + Chl, Cld + Gln to Pg + Chl + Qtz, and Gln + Jd + Qtz to Ab + Al-free Chl, we assign:

- assemblages containing Cld and/or Crp without Gln to the W assemblage;
- assemblages containing Cld and Gln to the X assemblage;
- assemblages containing Gln and/or Jd without Pg, Cld or Crp to the Y assemblage;
- Z assemblages are not relevant here.

These assemblages, as modified here, are further referred to as the W', X', Y' and Z' assemblages, corresponding to decreasing Al saturation of the rock. As a consequence, considering that the T-P conditions of the considered rocks fall over a very narrow variation range, a decrease of b_0 (and celadonite content) is expected from Y' → through X' → to W'. Assemblages Y' and X' are those in which we measured the mean b_0 range 9.038–9.042 Å (# 1 to 4 in Fig. 2 and Table 1), we considered above (section 4.1) as reference values for HP/LT metapelites, because they are comparable with the b_0 scale of Sassi & Scolarì (1974).

If the three, largely scattered, b_0 populations # 7 to 9 are temporarily disregarded for reasons explained below (in the section 5.3), the lower b_0 population # 6, when compared with curves # 1 to 4, fit the above expectation, being related to more Al-saturated mineral assemblages. The low mean b_0 value of only 9.032 Å for population # 5 does not reflect the low estimated metamorphic gradient of 12°C/km, but may partly reflect the fact that these samples are X' assemblages, whereas the Phe from the Diablo Range (# 3) are exclusively, and those from Sifnos, Nilüfer and Tavsanli Formations (# 1, 2, 4) predominantly, from Y' assemblages.

Further evidence of this effect is given by Arkai & Kovacs (1986), who ascribe the low average K-mica b_0 values of 9.024–9.027 Å in medium-high pressure metasediments of the lowest tectonic units of the Aggtelek-Rudabanya Mountains (NE Hungary) to “the possible b_0 -decreasing effect of the paragonite being present in small amounts”.

A gap of 0.021 Å occurs between the mean b_0 values from X' # 5 and W' # 6 assemblages, consistent with the prediction of Guidotti & Sassi (1976), and with the lower b_0 limit of 9.010 Å for the border between medium- and high-P metamorphism in Al-rich low-variance assemblages proposed by Francescellì *et al.* (1989). Such a wide gap may be specific to HP/LT terrains: a lower difference of 0.012 Å was found in the intermediate-P metamorphism of the Betic Cordilleras (Gomez-Pugnaire *et al.*, 1978), whereas this difference seems to disappear at low-P conditions: a difference of only 0.004 Å was found by Bossière *et al.* (1979) in the Grande Kabylie.

As regards chemistry, in all chemical diagrams the WKM from W' assemblages plot in the lowest celadonitic part of the distribution field of the data-points.

In contrast, the Phe from X' and Y' assemblages have higher Si and Fm contents. Note, however, that the Phe from the Schistes Lustrés, although all from W' assemblages, extend to 7.3 Si apfu and 1.23 Fm apfu, *i.e.*, celadonite contents as high as those from X' and Y' assemblages from the other HT/LP assemblages.

4.4 Relationship between b_0 and celadonite content

The b_0 values are plotted against two parameters measuring the celadonite content, Si apfu (Fig. 4) and Fm (Fig. 5). The chemical data mentioned a few lines above, on the Phe from the Schistes Lustrés from Agard *et al.* (2001), of which no samples for b_0 measurement were available, are plotted along the base for comparison of chemical contents. Both Fig. 4 and 5 show a linear regression with much scatter ($R = 0.80$ and 0.79 resp.). A second-order polynomial regression of the b_0 values *versus* composition yields slightly better correlations in both cases ($R = 0.82$ and $R = 0.81$). The polynomial regression we obtained for b_0 against Fm (Fig. 5) has a maximum b_0 value of 9.047 Å at Fm \approx 1.7, which is higher than that of equation 7 of Guidotti *et al.* (1992), *i.e.*, $b_0 = 9.042$ Å and Fm = 1.3 apfu. The two polynomials run very closely together up to about Fm = 1.2 at 9.042 Å, but progressively diverge at higher Fm values. Well aware of the paucity of our data-base, we speculate that this divergence, and the difference in the position of the maxima, are mainly due to the negative term 0.0285 Fm^2 in the equation of Guidotti *et al.*, which is negligible at small Fm values but becomes larger at higher Fm values, equalling 0.041 at Fm = 1.2. This difference between the two polynomials mainly reflects the virtual absence of Phe with Fm > 1.4 from both data-bases, and probably the paucity in our data-base of low-celadonite Phe with Fm 0.15–0.4, which are plentiful in the database used by Guidotti *et al.* (1992).

When attempting to combine our chemical and b_0 data, the effect of $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ on the b_0 parameter must be considered. This is somewhat difficult to assess, since the values of this ratio are unevenly distributed within the range of b_0 parameters and Si contents in our data-base: high $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ values are poorly represented among high- b_0 and high-Si WKM, but constitute the bulk of the lower- b_0 and lower-Si assemblage WKM. Moreover, Si contents higher than about 7.1 apfu are not represented in our data-

base. Still, high $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ ratios appear to decrease the b_0 parameter at low Si and Fm contents ($\text{Si} < ca. 7.1 \text{ apfu}$), and increase it at higher Si and Fm contents. Values of b_0 in the range 9.060–9.108 Å have never been reported for metamorphic Phe, but it is more than a coincidence that the b_0 vs. Si content curves for high $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ Phe extrapolate to the high value of the b_0 lattice parameter (9.108 Å) measured on sedimentary siliceous ferrocaldonite and ferroaluminocaldonite by Li *et al.* (1997).

All these problems may be clarified by merging our data base and that of Guidotti *et al.* (1992), and also considering the several analyses published in the last few years on natural and synthetic WKM. We are working on this topic in order to move from speculations to solid statements.

5. Further discussion on WKM b_0 values and celadonite contents in HP/LT terrains

In the final paragraph of section 4.1 we noted that the range and means of b_0 values from Phe from X'- and Y'-assemblage metapelites in most of the areas considered in the present paper are similar to those indicated by Iwasaki *et al.* (1978) for the glaucophanitic greenschist facies of the Sanbagawa belt, despite their notably higher metamorphic P/T gradients. On the other hand, a large scattering of b_0 values turns out in some cases.

A number of explanations for these two orders of problems may be considered:

- 1) the appearance of Fe-Mg-Al phases other than those ($\text{Ms} + \text{Chl} \pm \text{Bt} + \text{Ab}$) considered by Sassi & Scolari (1974);
 - 2) the effect of increasing metamorphic grade;
 - 3) re-equilibration of WKM compositions and b_0 values as a result of residence at lower-P and higher-T conditions during slow uplift;
 - 4) incomplete re-equilibration of WKM with maximum HP/LT conditions at low grades, due to brief residence times of rocks at subduction depths;
 - 5) inability of the b_0 method to discriminate, in the range of the HP metamorphism, between different HP/LT gradients, due to a non-linear relationship between b_0 and the celadonite content of Phe (whereby b_0 values reach a maximum).
- These five topics are discussed in the four points 5.1 to 5.4.

5.1 Appearance of other Fe-Mg phases

It is obvious that crystallisation of Fe-, Mg- and Al-bearing phases such as Crp, Cld, Jd *etc.* coexisting with Ms+Chl, necessarily affects the partition of Fe, Mg and Al among them and coexisting Chl and Ms. Therefore, further comments on the wide interpretative possibilities offered by this point are unnecessary.

5.2 Differences in metamorphic grade

Guidotti & Sassi (1976, pp. 112–114; Fig. 12) inferred a decrease in the celadonite (or b_0) content of WKM with increasing T at “high P”, later clarifying (1986, p. 372) that

they referred to a high-P facies series. However, on their plot of muscovite b_0 values on a P-T diagram (1986, Fig. 1, as modified and extended in D'Amico *et al.*, 1987, p. 449), HP/LT gradients of 10°C/km requires *expansion* rather than contraction of b_0 with increasing grade. Moreover, a metamorphic geothermal gradient of 15°C/km interpolated on Velde's (1965) diagram, showing the effect of T on the celadonite content of WKM coexisting with Kfs at various P's, reveals a virtually constant celadonite content with increasing grade. The same is true for a 10°C/km gradient on Massonne's (1995b, Fig. 4) P-T diagram, showing Si contents of Phe coexisting with Kfs, Phl and H₂O.

Of the HP/LT areas for which data are available, only two provide distinct metamorphic zoning: the Schistes Lustrés and Phyllite-Quartzite Unit of Crete. In the latter unit, there is a distinct *increase* in the mean Si content of Phe from eastern through central and western Crete to the Peloponnese with increasing grade, 6.26→6.34→6.40→6.60 Si apfu for all Phe and 6.28→6.34→6.40 Si apfu for Phe of the “critical paragenesis” Crp-Cld-Chl-Phe-Qtz (Theye 1988, pp. 21–22). In the Schistes Lustrés, the Si contents apfu of the eight ‘C1’ Phe coexisting with Cld range from 6.84 to 7.16, similar to or marginally higher than those of four ‘P’ and ‘A’ Phe coeval with Crp, which range from 6.70 to 6.96 (Agard *et al.*, 2001, Table). Hence, neither area provides any evidence of a decrease in the celadonite content of Phe with increasing grade: if anything, the opposite is the case.

It therefore appears that there is little evidence of a decrease in celadonite content with increasing grade of HP/LT metamorphism, in contrast with the statement by Guidotti & Sassi (1976, 1986) but consistent with the pattern of the iso- b_0 curves indicated in their P-T diagram (1986, Fig. 1, and its modified and amplified version in D'Amico *et al.*, 1987, Fig. 17.7, p. 449).

5.3 Incomplete re-equilibration of WKM composition during exhumation or during residence at P peak of subduction

In view of the extensive evidence for the formation and recrystallisation of Phe in late stages of the structural development of HP/LT rocks (*e.g.*, Okrusch *et al.*, 1978; Dalla Torre *et al.*, 1996a; Jolivet *et al.*, 1996; Agard *et al.*, 2001), it may be stated that the low WKM b_0 values found in some HP/LT terrains, notably Crete and the Peloponnese (# 6 to 9 in Table 1 and Fig. 2), reflect re-equilibration at lower P's and possibly higher T's during exhumation.

However, the b_0 values found for the various considered terrains show little relation to the extent of post-HP/LT re-equilibration from petrological studies of these areas. For instance, the well-documented effects of: (i) a second, greenschist-facies metamorphism on the blueschists of central Sifnos, resulting in the breakdown of Jd + Qtz (Okrusch *et al.*, 1978) and the extensive resetting of the radiometric ages of Phe of central Sifnos from 33–43 Ma to 24–21 Ma (Altherr *et al.*, 1979), and (ii) the compositional Phe-Ms gradients as a result of a “lower P and possibly higher T” overprint in the Diablo Range (Dalla Torre *et al.*, 1996a), are not reflected in markedly reduced b_0 values of the Phe from

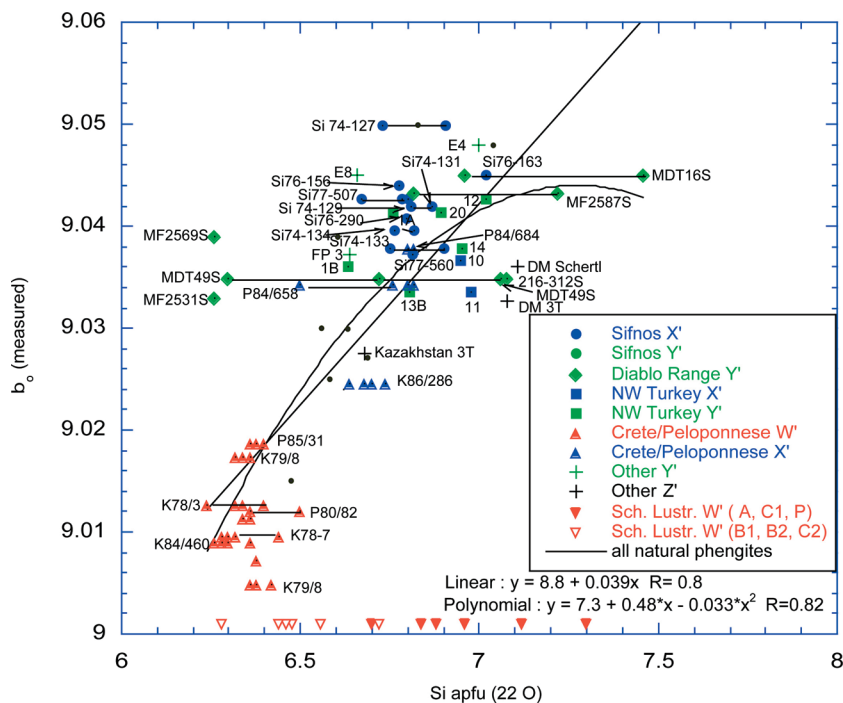


Fig. 4. b_0 values of studied HP/LT phengites plotted against Si content. Phengites from W', X', Y' and Z' are indicated in different colours (W' = red; X' = blue; Y' = green; Z' = black); different symbol shapes refer to different localities. Sample numbers are marked, except for most of W' assemblage phengites from Crete and Peloponnese. X', Y', W': see explanation in section 4.3.

Omitted are the following phengites: 7 and 9 of Fiorentini-Potenza (1969) and E6, E7, E9, E10 and E 11 of Ernst (1963), in view of poor quality of analyses (see section 3); WT04-8, 9, 15, 16 and 18 from north-west Turkey, the very fine grain of which did not allow EMP analysis. Nine phengites from Frey *et al.* (1983, Table 3), for which no assemblages are available, appear as additional very small dots and are included in the linear and polynomial regressions given for all natural phengites. Compositions of 13 phengites from Schistes Lustrés (Agard *et al.*, 2001), all from W' assemblages, for which no samples for b_0 determinations could be obtained, are shown along the base of plot for comparison.

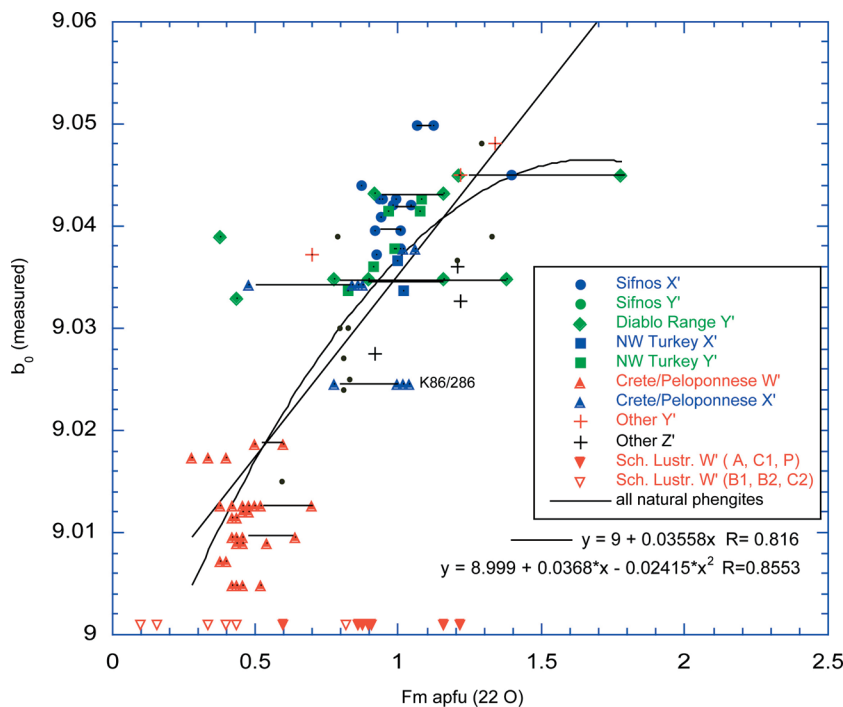


Fig. 5. b_0 values of studied HP/LT phengites plotted against Fm content (= Fe+Mg+Mn apfu). Sample numbers, colours, symbol shapes, and omitted analyses as in Fig. 4. Also indicated: the polynomial regression through b_0 values calculated using equation 7 of Guidotti *et al.* (1992).

these areas. In the Diablo Range, this absence of reduced b_0 values may possibly reflect the subordinate quantities of re-equilibrated WKM, since Dalla Torre *et al.*, reporting compositional ranges as broad as 6.1–7.7 Si apfu and 0.3–2.0 Mg+Fe apfu in the WKM of some samples (Dalla Torre *et al.*, 1996b, Fig. 4), consider these WKM to represent a physical mixture of numerous small Phe domains and smaller numbers of Ms domains.

In contrast, in the Schistes Lustrés, there is a distinct contrast between the high celadonite contents (6.7–7.3 Si apfu) of the early Phe cogenetic with Crp ('A') or Cld ('C1') or in-

cluded in Cld ('P'), and the low-celadonite contents (6.27–6.53 Si apfu) of Phe overgrowing Crp ('B1', 'B2') or associated with Chl replacing Cld ('C2') (Agard *et al.*, 2001, pp. 481–482; Tables 3 and 4).

Theye (1988, pp. 54–55, Fig. 13, 18) assigned widespread formation and recrystallisation of Ms in the Phyllite-Quartzite series of Crete and the Peloponnese to the late stage of, and subsequent to D2, the deformation phase associated with exhumation, partly replacing the characteristic HP/LT minerals Cld, Crp, alkali amphibole and Lws, which were mainly formed during a static period between defor-

Fig. 6. Different colours refer to five ranges of $Fe_{rel.}$, i.e. $Fe_{total}/(Fe_{total} + Mg + Mn)$, for natural Phe and the synthetic Mg-Phe in the range muscovite-aluminoceladonite of Schmidt *et al.* (2001). Different symbol shapes refer to phengites from W', X', Y' and Z' mineral assemblages (W' = large dots; X' = squares; Y' = diamonds; Z' = upright triangles; synthetic Phe = inverted triangles).

Each equation refers to the $Fe_{rel.}$ sample population shown in same colour. For sample numbers and omitted analyses, see Fig. 4.

Nine phengites from Frey *et al.* (1983, Table 3), for which the mineral assemblages are not known and which were shown in Fig. 4 and 5 as small dots, are included.

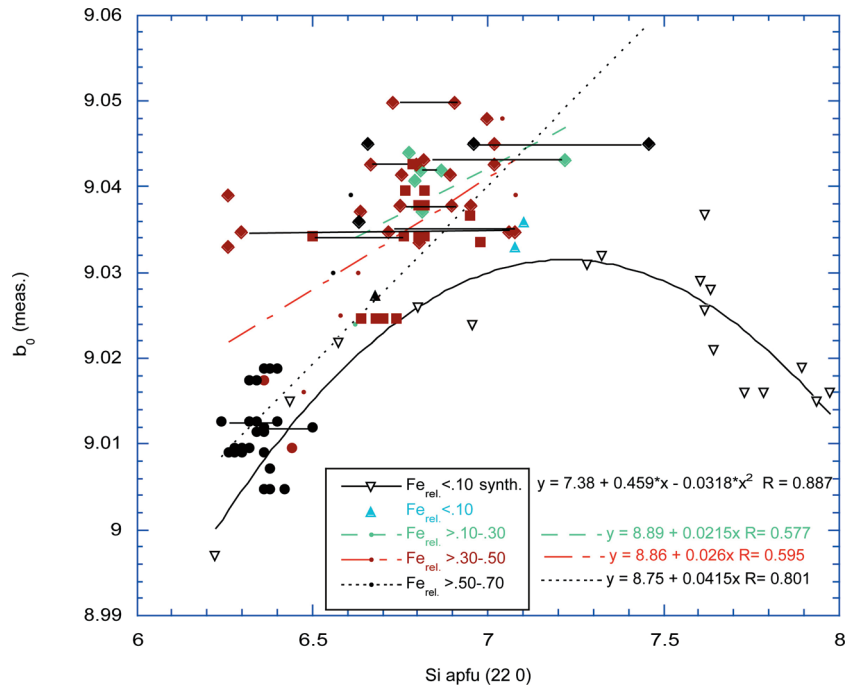
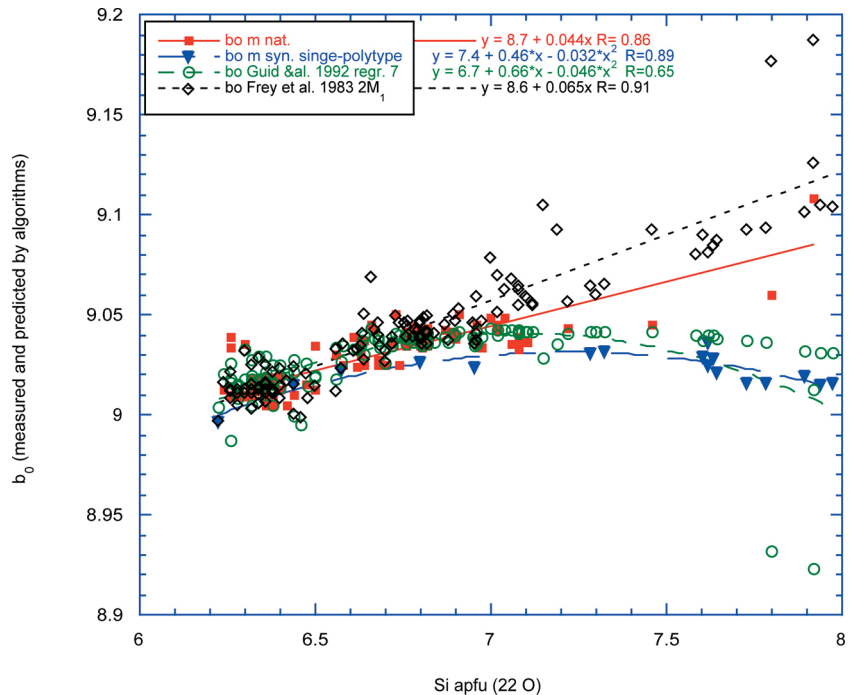


Fig. A1. Si content plotted against measured b_0 values, and the b_0 values predicted by equations of Frey *et al.* (1983) and Guidotti *et al.* (1992, equation 7), of the studied HP/LT phengites and the synthetic Mg-phengites in the range muscovite-aluminoceladonite of Schmidt *et al.* (2001). Values for the sedimentary ferroccladonite and ferroaluminoceladonite from Gavenwood Tuff, New Zealand (Li *et al.*, 1997) and the Wind River ferroccladonite (Wise & Eugster, 1964) are included in regressions.



mation phases D1 and D2. However, he reports that evidence for D2 is lacking in many localities.

Jolivet *et al.* (1996) distinguished two cooling regimes on the basis of the extent of Crp preservation in the Phyllite-Quartzite series of Crete: a very fast decompression regime, during which most of the cooling occurred at relatively high P, and a slower decompression regime, when the rocks were initially isothermally decompressed and finally cooled at low P's. However, at least on E Crete (Tilden, 2003; Kisch & Tilden, 2004), the difference between the b_0 values of Phe from these two regimes appears to be very small. Formation

or recrystallisation of all or most of the Phe in the Phyllite-Quartzite series is very unlikely in view of: (i) the very rapid exhumation documented for W Crete (Thomson *et al.*, 1998, 1999; see section 2); and (ii) the improbability of ascribing the very low b_0 values from the lowest grades of the HP/LT metamorphism on E Crete – where no Cld and only rare Crp formed – to retrogradation at lower P and/or higher T. Thus, re-equilibration is insufficient as an explanation for the low b_0 values of Phe.

In view of the evidence of brief residence and very rapid exhumation on W Crete, Kisch & Tilden (2004) and Kisch

(2004) argue for brief residence at the HP/LT metamorphic conditions as the cause of the low b_0 values of Phe in the Phyllite-Quartzite Unit of Crete and the Peloponnese in general, and in the LT part on E Crete in particular (scattered b_0 populations # 7 to 9).

5.4 Inability of the b_0 method to discriminate, in the range of HP metamorphism, between different values of HP/LT metamorphic gradients

The approach adopted here is based on the assumption that the WKM considered are truly dioctahedral, in which the amount of R^{2+} apfu is equal to Si apfu – 6 (in a formula unit based on 22 oxygen atoms). Therefore, Fe^{2+} apfu (calc.) = $R^{2+} - Mg$ apfu = Si – 6 (Si apfu – 6) – Mg apfu.

The values of b_0 in celadonite-rich Phe appear to be closely dependent on their Fe^{2+} (calc)/(Si – 6) ratios, low- Fe^{2+} Phe having low b_0 values, and higher b_0 values being expected only in Fe^{2+} -rich Phe. This has important implications for the use of Phe b_0 in characterizing high HP/LT metamorphic gradients.

So far, b_0 values higher than 9.050 Å have not been found in Phe from HP/LT metapelites. Most of the WKM considered in this paper, including those of the W' assemblages from CW Crete and the Peloponnese, have Si contents between 6.2 and 7.1 apfu, and divergence between the b_0 values of high- and low- Fe^{2+} Phe is relatively small (Fig. 6). However, some of the Phe from the Schistes Lustrés and Diablo Range contain up to 7.5 Si apfu, with a general decrease to intermediate and low values of Fe_{rel} (= $Fe_{tot}/[Fe_{tot}+Mg+Mn]$) with increasing Si apfu (Fig. 6). It is therefore possible that the relationship between b_0 and celadonite content is not linear, so that the b_0 values reach a maximum.

Inasmuch as the b_0 values of high-celadonite Phe can be expected to be high only for high Fe^{2+} contents, our samples do not have high b_0 values: high b_0 values are to be only expected in Fe^{2+} -rich high-celadonite Phe, and chemical analysis is required to establish whether the Phe is Fe-rich. Since the b_0 method is commonly used for characterizing the metamorphic P/T gradient without the need for chemical analyses, the conclusion can only be that the method cannot be used to discriminate different P/T values **in the range of high metamorphic P/T gradients**, in which the occurrence of Fe-rich celadonite-rich Phe is predictable. Fortunately, such rocks commonly bear mineral phases that reveal their HP/LT nature without requiring special analyses other than simple optical microscopy.

6. Conclusions

The phengites of the metapelites considered in the present paper, selected from areas with metamorphic P/T gradients higher than those in the two HP terrains considered by Sassi & Scolari (1974), are appropriate for characterizing WKM from high-P metapelites. The present chemical and b_0 study allows the following conclusions to be stated.

1. As expected from Guidotti & Sassi (1976), both chemistry and mean b_0 values turn out to be controlled, at any set

of P-T conditions, by the mineral assemblages, and particularly by the extent of Al saturation with reference to the AK-Na system. Assemblages W, X, Y, Z, defined by the above authors in order of decreasing Al saturation, have been broadened in the present paper to accommodate the occurrence of the typical minerals occurring in HP/LT rocks. Hence:

- assemblages W' are those containing Cld and/or Crp without Gl;
- assemblages X' are those containing Cld and Gl;
- assemblages Y' are those containing Gl and/or Jd without Pg, Cld or Crp;
- assemblages Z' are those not containing the above Al-phases.

2. As the b_0 scale of Sassi & Scolari (1974) is related to bulk compositions of assemblage Y very close to X, the reference b_0 values for the HP/LT metamorphism have been taken from assemblages X' ± Y'. They all range around 9.040 Å, a value which is proposed here as a reference for WKM in HP/LT metapelites. This narrow b_0 range may indicate that the increase in mean b_0 of Phe in metapelites reaches a maximum in HP/LT metamorphism.

3. Contrary to original expectations, these values are lower than that of 9.054 Å reported by Sassi & Scolari (1974) for the Daday-Ballidag area and 9.056 Å for the Sanbagawa belt of Shikoku, in both cases apparently from predominantly metabasic rocks. They still only fall in the lower part of the 9.032 < b_0 < 9.054 Å range subsequently extrapolated from the measured mean value of 9.032 Å by Iwasaki *et al.* (1979) for metapelites of the Sanbagawa belt.

4. The Phe from W' assemblage of the Phyllite-Quartzite Unit (# 5 in Table 1) show mean b_0 values some 0.021 Å lower than those from less Al-rich X' assemblages of the same Unit (# 6). A large difference between the b_0 mean values of X vs. W assemblages appears to be specific to HP/LT terrains.

5. From the chemical viewpoint, the most striking features of these HP/LT WKM are the important extent of celadonite substitution and, consistently with Guidotti & Sassi (1976, 1986, 1998a), its dependence on mineral assemblage. Micas from W' assemblages always plot in the lowermost celadonite field. Considering chemistry and b_0 values jointly, the investigated WKM Phe of the W' and X' + Y' assemblages constitute two quite well-constrained populations: the Phe of W' assemblages with Si-contents of 6.25 to 6.50 apfu and b_0 parameters of 9.005 to 9.019 Å; and the Phe of X' + Y' assemblages with Si contents of predominantly 6.6 to 7.1 Si pfu and b_0 parameters of 9.025 to 9.050 Å.

6. The b_0 values from one of the two HP/LT areas with distinct metamorphic zoning, the Phyllite-Quartzite Unit, increase with metamorphic grade; in the other, the Schistes Lustrés, celadonite contents remain the same or increase only marginally. This behavior does not support earlier suggestions by Guidotti & Sassi (1976, 1986) that the b_0 parameter from HP/LT terrains decreases with metamorphic grade, but it is consistent with the pattern of the iso- b_0 curves in the HP/LT part of their P/T diagram (1986, Fig. 1, amplified and modified in D'Amico *et al.*, 1987, Fig. 17.7, p. 449).

7. It has been observed earlier that the Phe from Sifnos appear to have higher b_0 values than those from the Tavsanli

area and from central and W Crete and the Peloponnese, but for a similar range of Si contents. An obvious explanation for that difference in b_0 is that the b_0 values of high-Si, high-Fm Phe may depend on other compositional features in addition to Si and Fm contents. Among these factors, the $\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ ratio of Phe should be considered.

8. The evidence for re-equilibration by crystallisation and/or recrystallisation of Phe at higher T and lower P during exhumation is equivocal. Radiometric-age evidence for re-equilibration of WKM during a later greenschist overprint in Sifnos is not reflected in reduced celadonite contents or b_0 parameters, and re-equilibration of the Phe during exhumation in the Diablo Range is not reflected in reduced b_0 parameters; whereas the Phe crystallised during later deformation phases in the Schistes Lustrés show significantly lower celadonite contents than the HP/LT Phe. In the Phyllite-Quartzite Unit of Crete and the Peloponnese, the effect of re-equilibration is probably small.

9. In interpreting the relation between the b_0 values of HP/LT terrains and related metamorphic gradients, the effects of several factors should be considered, including: (i) subduction rate and residence time vs. the kinetics of HP/LT metamorphic reactions, and (ii) the role of the precursors of Phe in HP/LT rocks, which may be either the result of chemical adjustment of WKM older than the HP/LT metamorphism or, more probably from the energetic viewpoint, Phe newly nucleated during HP/LT metamorphism.

10. The highest mean b_0 value, 9.042 Å, is found for the Sifnos Phe, with a geotherm of 5–10°C/km for the HP event, but Phe's from the Tavsanli area (NW Turkey), with a similarly high metamorphic P/T gradient estimated to be 5°C/km, have a lower mean value of 9.038 Å, identical to that of the Diablo Range with a higher estimated metamorphic gradient of 14°C/km.

Therefore, the b_0 method is unable to discriminate between different HP/LT regimes within the HP metamorphic range, mainly due to crystal-chemical problems. Furthermore, comparative b_0 interpretations of different HP/LT sample populations from various belts are impeded by poor understanding of the extent of re-equilibration at LP/HT during exhumation. These conclusions, however, do not weaken the validity of the b_0 method for medium- and low-P/T gradients and for detecting generic HP metamorphism.

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Appendix

Comparison of measured b_0 values of phengites with b_0 values calculated using the equations of Frey *et al.* (1983) and Guidotti *et al.* (1992)

The b_0 values measured on the studied Phe are shown in Fig. A1, together with those calculated using equation 7 of Guidotti *et al.* (1992) and that of Frey *et al.* (1983) for $2M_1$. The equation of the former authors systematically overestimates the b_0 of synthetic Phe over the whole range of Si apfu values by ≈ 0.010 Å (for low Si apfu) to 0.020 Å (for high Si apfu). Instead, it grossly underestimates the b_0 values of the Fe-rich sedimentary celadonites – ferroceldonite and ferroaluminoceldonite (Li *et al.*, 1997) by as much as 0.20 Å, and the less iron-rich Wind River celadonite (Wise & Eugster, 1964) by 0.10 Å. Both of the above behaviours reflect the fact that the equation of Guidotti *et al.* is based on Phe with an average $\text{Fe}^{2+}/(\text{Si}-6)$ ratio, and therefore tends to overestimate the b_0 of Fe-free Phe and underestimate that of Fe-rich celadonites. For the b_0 values of Phe in the $\text{Fe}^{2+}/(\text{Si}-6)$ ranges > 0.30 – 0.50 and > 0.10 – 0.30 , regression for the predictions of Guidotti *et al.* corresponds reasonably well with that for the b_0 values measured for Phe in these ranges and up to ca. 7.1 Si apfu.

The regression of Frey *et al.* (1983) for polytype $2M_1$ even more strongly overestimates the b_0 of synthetic Phe – progressively so for higher Si apfu contents, as a result of the linear regression. It also grossly overestimates the b_0 of the Wind River celadonite (Wise & Eugster, 1964), but gives an excellent estimate of the b_0 of ferroceldonite and ferroaluminoceldonite (Li *et al.*, 1997).

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