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DENSITY LIMITS OF RECRYSTALLIZATION INFERRED FROM ROCK GLASSES

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ABSTRACT

Plot of densities (ρ_{ROCK}) versus packing index of the metamorphic rocks (ϕ_{ROCK}) and their glasses gives the lines with the slope of a = 21.6 ± 0.28. This revealed slope in combination with density and packing index data determines the rock *densification trajectory*, *densification index* (D.I.) and rock *density limits*. The associated rock volume changes may be modelled and their crustal limits approximated. The studied metapelites have the density range of 2.69-2.86 g/cm^3 and their corresponding rock glasses 2.40-2.62 g/cm^3. Packing indices for these rocks are ϕ = 59.1-60.9 and for their fused glasses ϕ = 54.0-56.3 % . Maximum *density limit* for these rocks is estimated to be ~ 3.2 g/cm^3, and 17 % associated volume reduction.

KEYWORDS: rock density limits, rock glasses, packing index, volume change

INTRODUCTION

Progressive metamorphic rock recrystallization is, in first approximation, an isochemical process associated with appearance of new equilibrium phases, redistribution of chemical components and rock dehydration. Accompanied volume changes during metamorphic reactions progress thus attribute to the changes in metamorphic rock density.

French (1976) emphasised the importance of the relationship between silicate rock density and composition of igneous and metamorphic rocks. His empirical density formula

$D_C^F = 2.6[2N_o/(4N_{Si} + 3N_{Al})]^{1/2}$, where N_{si} and N_{Al} is the number of Si and Al atoms on the one oxygen (N_o) basis, has been used as a factor equivalent to 'normative' rock density. Comparison of this calculated 'normative' density based on the bulk chemical composition of a particular rock with its measured density offered the specific data for metamorphic pressures and temperatures evaluation (Fig. 1). Changes of *p-T* and the reaction recrystallization progress cause the volume changes and the reaction products have eventually higher density with respect to the former mineral assemblage. Calculated 'normative' rock density using anhydrous basis remains however the same. Thus the densification of a metamorphic rock runs on its specific composition trajectory attaining consequently higher packing index in the metamorphic reaction products.

In the present model it has been presumed, that if chemical composition of metamorphic rock, its density and the reference density unit are known, the rock density change may be assessed and the specific densification rock trajectory numerically approximated.

The fused rock glass, has been chosen as a density reference unit. Its measured density has been compared with the density calculated from the molar volumes of the rock forming oxides. This approach enables to follow the density range for a particular metamorphic rock and makes possible to expect the density limits based on the presumed atom packing in the rock.

METHODS AND MODEL

The powdered and homogenised metapelitic rock samples were melted in the quenching furnace in argon atmosphere for 4 hours at 1200 ^{o}C and atmospheric pressure. No major chemical changes have been expected. The densities of fused rock glasses and rocks have been determined by sink-float method (see e.g. Proks, 1974; Fletcher, 1979; Hey, 1979). Bromoform ($CHBr_3$, ρ = 2.885 g/cm^3, n = 1.598) and methanol (CH_3OH, ρ = 0.792 g/cm^3, n = 1.328) form an ideal liquid solution and index of refraction of this mixed liquid allows direct reading of its density compared to floating or sinking of the sample. Reproducibility of a measurement was in the range of ± 0.006 to 0.01 g/cm^3. Standard deviation (S) obtained from 15 measurements represents simultaneously the rock homogeneity. The metapelites consisted of *Qtz* (~25-43 mod.%), *Bt* (~20-28), *Ms* (~12-30), *Pl* (~15-35), *St* (~1-4), *Grt* (~1-3), *Sil* (~1-2 mod %). Their density data are given in Tab. 1.

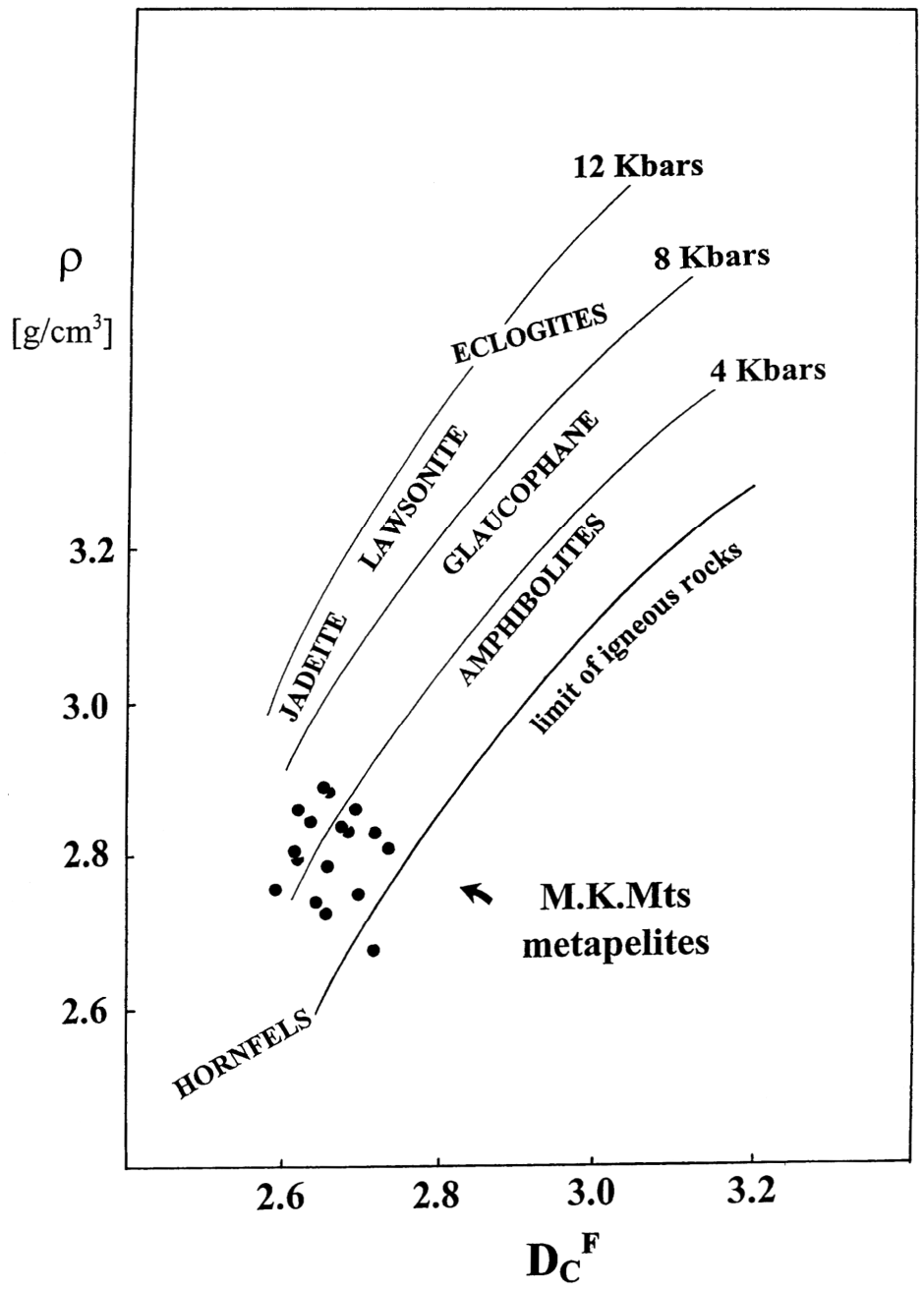

Fig. 1 Increasing metamorphic pressures produce mineral assemblages with higher overal density. As the metamorphic recrystallization is dominantly isochemical, the French density reference unit $D_C^F = 2.6[2N_o/(4N_{Si}+3N_{Al})]^{1/2}$ calculated on the anhydrous one oxygen basis remains unchanged. Redrawn according to French (1976).

Table 1 Densities of the Malé Karpaty Mts. metapelites (ρ_{ROCK}, g/cm^3), their fused rock glasses (ρ_{GLASS}), calculated non crystalline solid units (ρ_{NCS}), corresponding packing index (ϕ) and densification index (D.I.).

Sample	ρ_{ROCK}	ρ_{GLASS}		D_C^{F*}	ϕ_{ROCK}	ϕ_{GLASS}	ϕ_{NCS}	D.I.
2.	2.75 ± 0.02	2.48	2.50	2.72	60.8	54.9	55.3	0.39
4.	2.80 ± 0.02	2.57	2.55	2.74	61.2	56.0	55.7	0.37
5.	2.70 ± 0.01	2.47	2.49	2.73	59.7	54.6	55.1	0.33
6.	2.69 ± 0.02	2.49	2.48	2.70	59.7	55.2	55.1	0.30
7.	2.76 ± 0.03	2.57	2.57	2.77	60.0	55.7	55.8	0.30
8.	2.74 ± 0.01	2.54	2.55	2.75	59.8	55.5	55.7	0.29
9.	2.80 ± 0.05	2.59	2.60	2.77	60.5	55.9	56.1	0.33
11.	2.74 ± 0.03	2.49	2.52	2.71	60.4	54.4	55.4	0.38
12.	2.75 ± 0.02	2.61	2.62	2.77	59.1	56.1	56.3	0.22
14.	2.79 ± 0.01	2.56	2.56	2.73	60.9	55.8	55.7	0.36
17.	2.86 ± 0.05	2.55	2.54	2.74	62.5	55.7	55.7	0.47
18.	2.75 ± 0.02	2.54	2.55	2.77	60.2	55.5	55.7	0.32
19.	2.69 ± 0.03	2.40	2.42	2.70	60.5	54.0	54.4	0.41
KB-1.	2.78 ± 0.04	2.55	2.55	2.73	60.8	55.7	55.7	0.36
KB-2.	2.79 ± 0.08	2.56	2.57	2.75	60.7	55.8	55.9	0.35
KB-3.	2.72 ± 0.02	2.56	2.55	2.73	59.5	55.8	55.7	0.26
KB-4.	2.75 ± 0.02	2.59	2.60	2.76	59.6	56.0	56.1	0.26
KB-5.	2.82 ± 0.04	2.62	2.63	2.78	60.5	56.3	56.4	0.31

* D_C^F is density calculated according to French (1976) formula $D_C^F = 2.6[2N_o/(4N_{Si}+3N_{Al})]^{1/2}$.

The density of the particular rock sample (ρ_{ROCK}), its fused rock glass equivalent (ρ_{GLASS}) and effective ion diameters given by Shannon and Prewit (1969) were used as the basic enter data for packing index calculations of rock (ϕ_{ROCK}), fused rock glass (ϕ_{GLASS}) and calculated non-crystalline solid (NCS) equivalent (ϕ_{NCS}).

As the uncertainty in co-ordination number for certain ions in rock and glass persists (e.g. Al^{IV} and Al^{VI}), the same ion volumes have been used for simplified comparison. For density calculation of the non-crystalline solid (ρ_{NCS}), the recalculated molar volumes of rock forming oxides of Bottinga et al. (1982) and their formula

$$\rho_{NCS} = \sum_{i=1}^{n} M_i X_i / \sum_{i=1}^{n} V_i X_i \quad (1)$$

has been used (Tab. 2). M_i stands for molecular weight, X_i for mole fraction and V_i for molar volume of the oxide *i*. The molar volume (V_m) of glass may be computed from the composition by means of equation

$$V_m^{GLASS} = V_i X_i + V_j X_j + \ldots = \sum V_k X_k \quad (2)$$

where V_i is the molar volume of a component *i* and X_i is its mole fraction. The average molar weight of glass (W_m) is expressed as the sum of mole fractions X_k multiplied by molecular weight of the particular oxide (W_k) in the system:

$$W_m^{NCS} = \sum W_k X_k \quad (3)$$

As the correlation between measured densities of the fused rock glasses (ρ_{GLASS}) and calculated densities of NCS (ρ_{NCS}) is high (Fig. 2), the model approach resulted thus in the calculation of the model rock properties.

Bulk chemical analyses of the metapelitic rocks were recalculated to the unit cell formulas based on 160 oxygens (Appendix I). The rock formulas have been used later for determination of volume/oxygen (*V/Ox*) and volume/atoms (*V/Atoms*) ratios. The *V/Ox* value for numerous minerals is plotted against *V/Atom* (Fig. 3). Many minerals of the same chemical composition fall along the straight lines (e.g. And-Sil-Ky, SiO_2- modifications, Cc-Arg, An-An_{GLASS}, Di-Di_{GLASS}) with the same slope as it could have been predicted. Almost all minerals studied, metapelitic rocks and their corresponding glasses plotted in density and packing index co-orditates fall on the lines with the same slope (Figs. 4, 5). This revealed arrangement is considered to have an important petrologic significance. As the origin of lines with the same slope has not been completely understood,

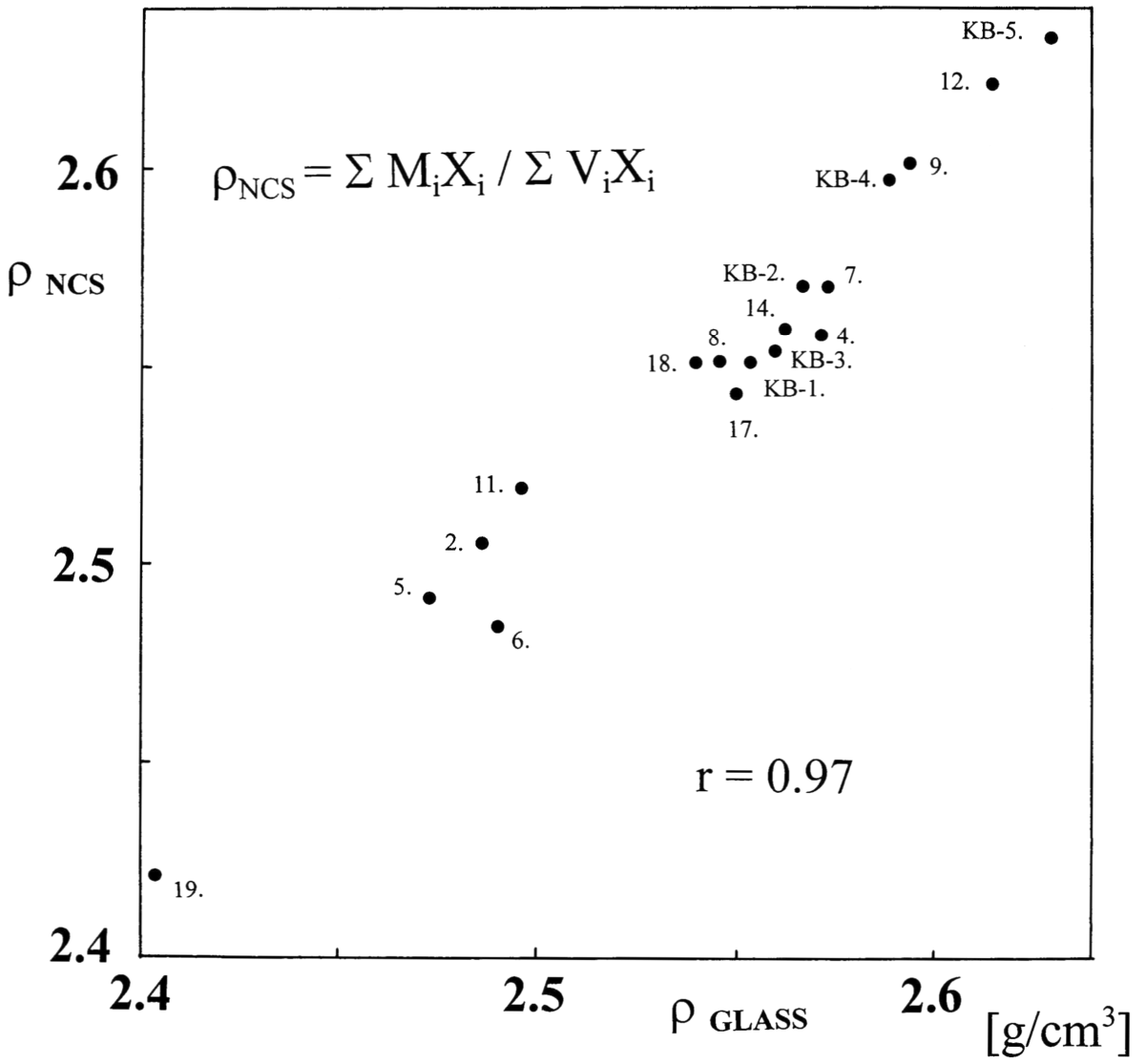

Fig. 2 The measured glass density data (ρ_{GLASS}) and densities of the rock glasses calculated (ρ_{NCS}) on the basis of molar volumes of the rock forming oxides in Tab. 2. and formula (1), give the high correlation (r = 0.97). The numerical approach may serve as a good density approximation within a broader range of metamorphic bulk rock chemical composition.

further studies have been made here to interpret the meaning of this slope.

The reactants of the low grade metamorphic reaction

$$7\ Ms + 6\ Chl = 6\ St + 7\ Bt + Grt + 3\ Qtz + 18\ H_2O \quad (R1)$$

have overall density of 2.71 g/cm^3. After the reaction has been completed the density change is $\Delta\rho$ = 0.62 g/cm^3, what corresponds to the volume reduction of 18.6 %. Reaction progress accompanied with water release represents significant volume change at the crossing of the isoreaction line. However, the extent of the volume change may not indicate the metamorphic grade as the protolite mineral assemblage has a significant contribution to the volume changes in rock.

If the model rock I1, I2 and I3 with different modal Ab/Qtz ratio is subjected to recrystallisation according to the reaction

$$Ab = Jd + Qtz \quad (R2)$$

the different modal composition gives different volume reduction in the rock as the density and packing index change (see Fig. 5)

I1 Ab 20 Qtz 80→Qtz 85.4 Jd 14.6 ΔV = 3.6 %
I2 Ab 40 Qtz 60→Qtz 70.9 Jd 29.1 ΔV = 7.7 %
I3 Ab 60 Qtz 40→ Qtz 56.3 Jd 43.7 ΔV =10.8 %

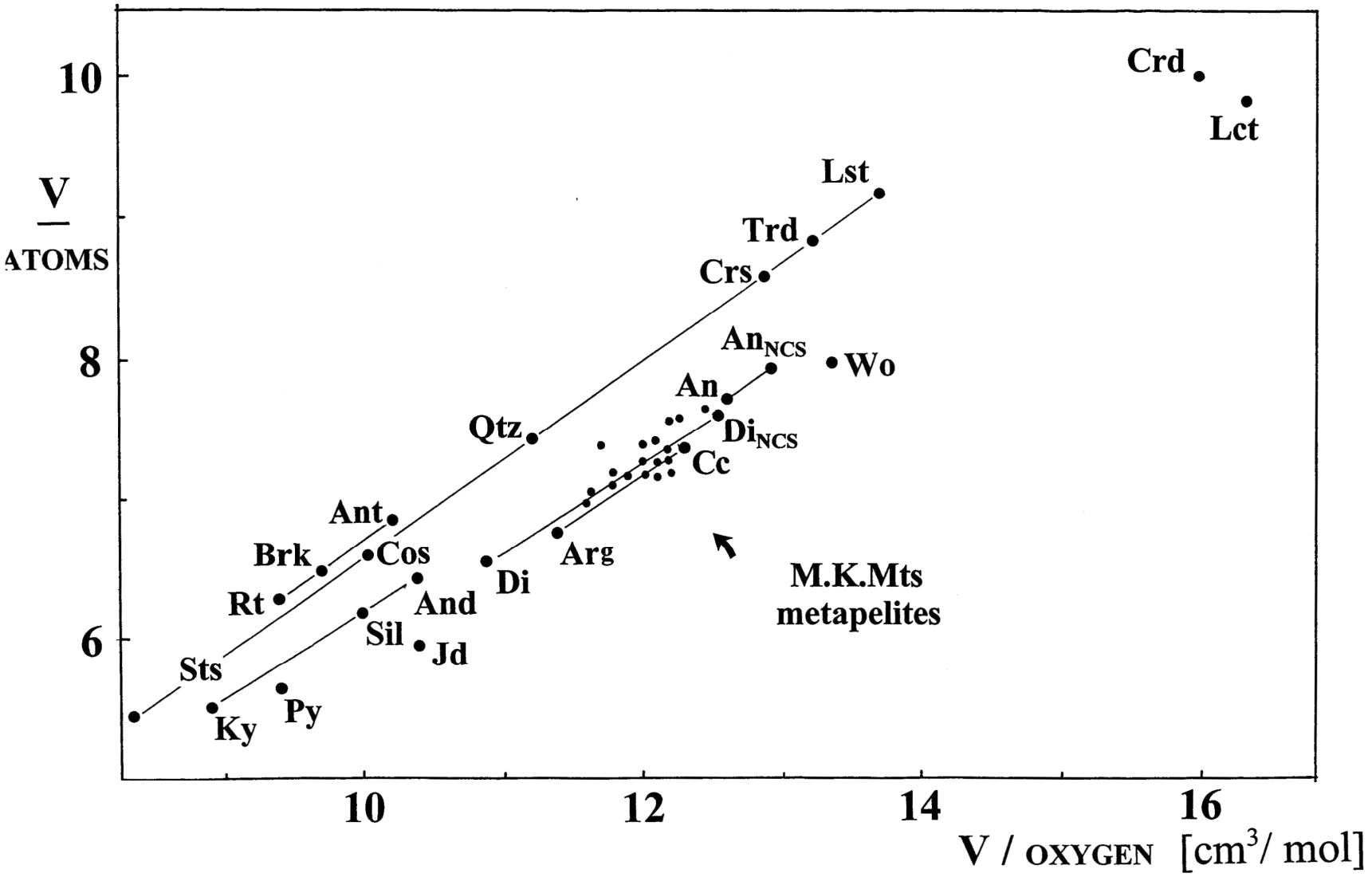

Fig. 3 High pressure and temperature phases tend to have denser atom arrangement with a high packing index. Isochemical solids with different structures have in *V/Oxygen* versus *V/Atoms* co-ordinates a similar slope, see e.g. andalusite (And) – sillimanite (Sil) – kyanite (Ky); Anatas (Ant) –brookite (Brk) – rutil (Rt).. that expresses the tendency of structure densification The studied metapelites represent rocks of lower to higher amphibolite facies with different modal amount of index minerals giving thus the scattered projection points. Mineral abbrevation according to Kretz (1983): albite (Ab), anorthite (An), Åkermanite (Åk), biotite (Bt), aragonite (Ar), calcite (Cc), chlorite (Chl), coesite (Cos), cordierite (Crd), cristobalite (Crs), diopside (Di), garnet (Grt), jadeite (Jd), leucite (Lct), lechatelierite (Lst), muscovite (Ms), staurolite (St), pyrope (Py), stishovite (Sts), tridimite (Trd), wolastonite (Wo), quartz (Qtz).

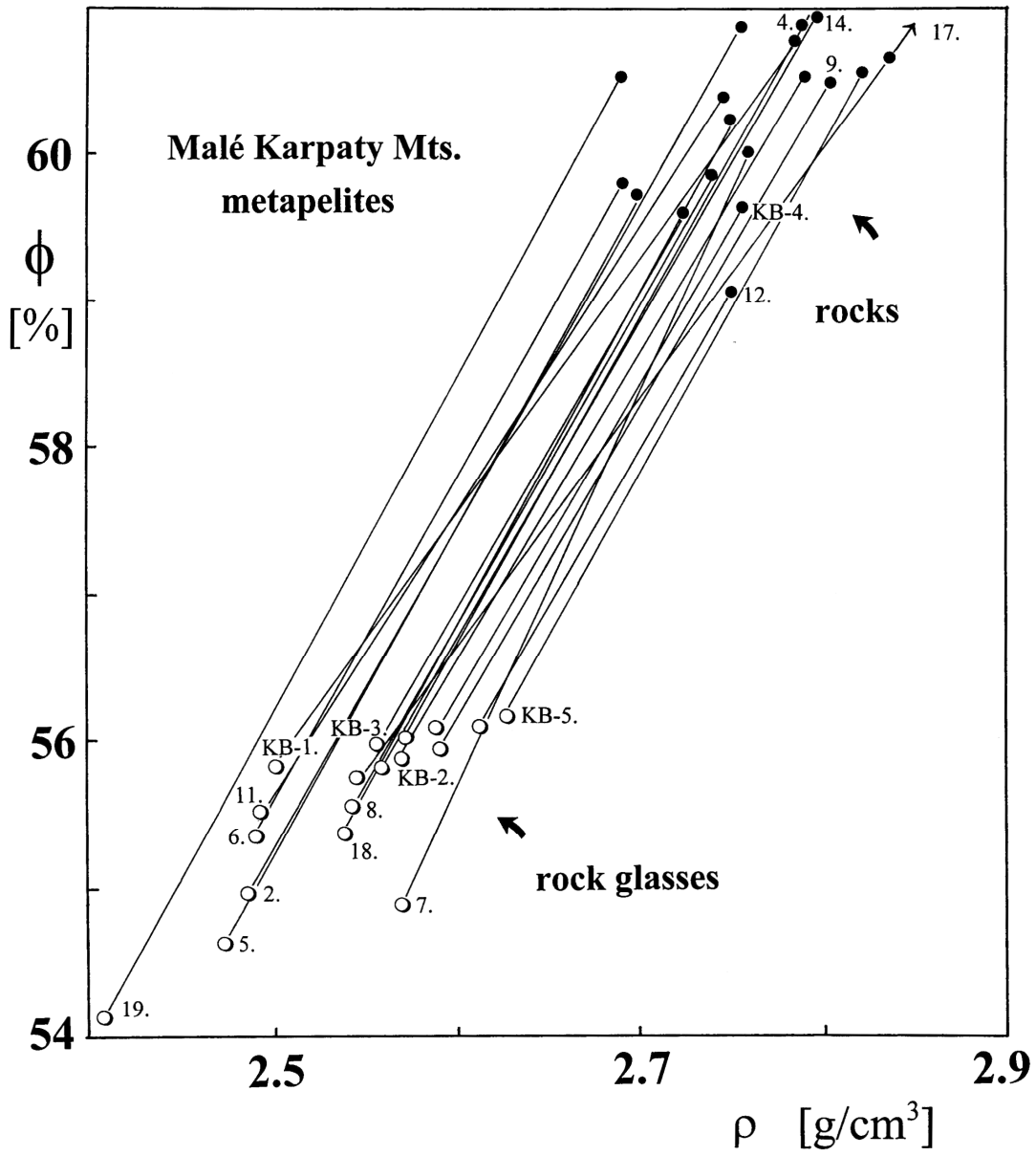

Fig. 4 Relation between density (ρ) and packing index (ϕ) of Malé Karpaty Mts. metapelites (●) and their glasses (○) is characterized by almost the same slopes. Packing index of the solids is given by their chemical composition and density. The present scattering of the rocks and corresponding glasses is predestined by the protolit mineral composition and the extent of the metamorphic reactions in particular rocks. The corresponding glasses represent the minimum density and packing index for their chemical composition. For the studied metapelites that recrystallized at higher temperatures and pressures (Dyda, 2002) packing indices are tending upwards. The value $\phi \approx 60.0$ represents 60% of 'space' filled by ions, the rest is the 'empty space' in the structure.

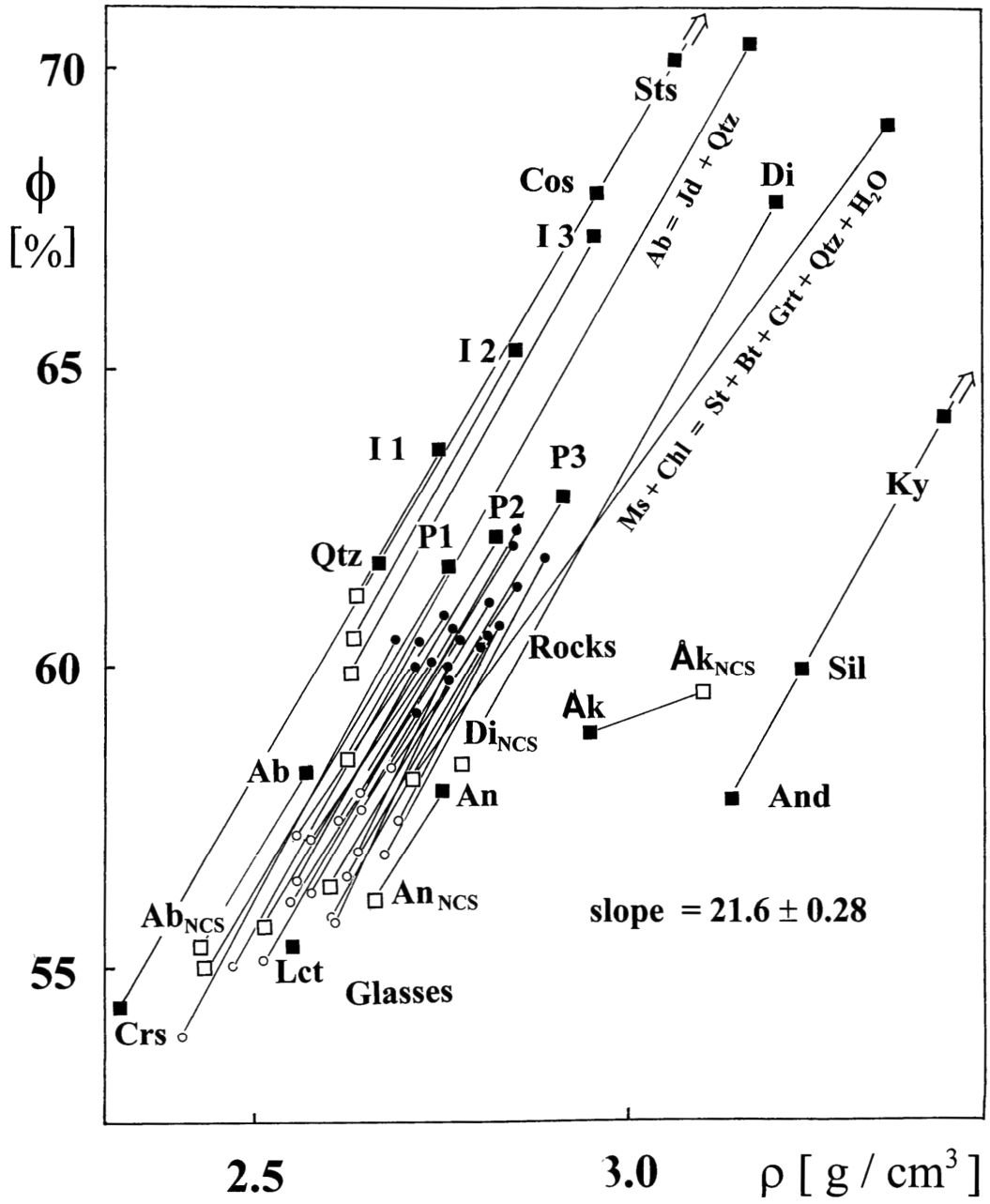

Fig. 5 The slopes of the lines $a = 21.6 \pm 0.28$ given by ρ and ϕ of the rocks and their glasses are followed by the rocks of different modal composition (I1-20Ab 80Qtz, I2-40Ab 60Qtz, I3-60Ab 40Qtz), model metapelitic rocks (P1, P2, P3), different minerals (■) and their glasses (□). The polymorphic modifications (SiO_2, TiO_2, Al_2SiO_5) have the same slope as well. Åkermanite glass ($\rho = 3.05$ g/cm^3) is denser than cristalline Åk ($\rho = 2.94$).

Table 2 Molar volumes (V_m, cm3/mol) of the rock forming oxides recalculated from V_m data of Bottinga et al. (1982) and used for ρ_{NCS} calculation*.

	V_m		V_m
SiO_2	26.40	MgO	10.21
TiO_2	10.78	CaO	12.71
Al_2O_3	36.42	Na_2O	18.50
Fe_2O_3	24.44	K_2O	23.02
FeO	10.35	Li_2O	11.97
MnO	11.14	ZnO	5.42

* Based on the presumption that density and coefficient of thermal expansion of the particular rock forming oxide vary in a regular fasion within the studied bulk chemical composition. The data make the base for density calculation and may cover a wide range of rock glasses.

The more complex metapelitic assemblage with modal composition 58 mod.% Chl, 36 mod.% Ms and 6 mod.% Qtz corresponds with the reactants of the reaction

$$Chl + Ms + Qtz = Crd + Bt + Al_2SiO_5 + H_2O \qquad (R3)$$

After completing the reaction the density changes from 2.73 to 2.81 g/cm^3. With increased pressure cordierite may eventually decompose to 61 mod.% Alm, 27 mod.% Sil and 12 mod.% Qtz and the volume decrease is 32 %. In the presence of Bt, cordierite decomposition may proceeds according to reaction

$$Crd + Bt = Alm + Kfs + H_2O \qquad (R4)$$

and from the previous Chl+Ms+Qtz assemblage the new one with Alm+Kfs+Sil is produced. The relevant volume change is 20.4 %. However, these progressive reactions are far more complex in nature, determined by original complex mineral assemblages and leading to the volume reduction of the rock. Clearly, rocks with simple mineral compositions are less suitable in this approach than the polyphase mineral assemblages. Consequently, more suitable are the rocks with the complex mineral reaction changes and solid solution phenomena. Progressive recrystallization brings thus the rocks to significant 'empty space' reduction and denser mineral rock structures.

The presumption of the present model is that the given rock approaches on its *densification trajectory* its density maximum given by the mineralogical composition and the packing index. The minimum reference density of a rock is defined by the non-crystalline solid unit (ρ_{NCS}). The ρ_{NCS} is obtained here numerically according to equation (1) using recalculated molar volumes of the rock forming oxides (Tab. 2). The measured densities of rock glasses (ρ_{NCS}) are in good agreement with the calculated density values see (Fig. 2, Appendix II.) and have high correlation (r = 0.97) approving thus the reliability of the calculated ρ_{NCS} in metapelitic rock compositions.

The ρ_{NCS} value and the determined densification trajectory slope (a = 21.6 ± 0.28) in density and packing index co-ordinates (Fig. 5) determines the density changes in metamorphic mineral assemblages.

If dense rock structure with packing index $\phi \approx 70$ is taken to be the limit and the density minimum is given by calculated ρ_{NCS}, then the rock *density limits* may be assessed by approximation (Fig. 6). With increasing of metamorphic temperature and pressure the whole rock reaction progress shifts the recrystallizing rock to the higher density and packing index. The *a/b* ratio on the specific densification trajectory, coined as the *densification index* (D.I.), expresses the distance of the metamorphic rock from its density limits given by the dense atom packing in rock structures. Thus for the studied metapelitic rock e.g. N^o 17., D. I. = (62.5-55.7) / (70-55.7) = 0.47.

Density of the rock as well as packing index alone need not indicate the attained degree of the metamorphic grade. However, both ρ and ϕ of the rock combined with ρ and ϕ of the corresponding glasses obtained on experimental and/or numerical basis may be a useful maximum volume change indicator for a given rock.

DISCUSSION

The attempts to calculate glass density from composition has been known for long in glass industry. Many distinguished authors see e.g. Baillie (1921), Gehlhoff and Thomas (1926), Huggins and Sun (1943), Demkina (1958), Rawson (1981), approximated successfully the relations between composition and density in glassy silicate systems.

Glass structure missing the long-range order and periodicity is difficult to describe with a simple comprehensive model (see e.g. Nicodemi and Coniglio, 1997; Brow, 2003; Buchenau, 2003; Pilla et al., 2003). Therefore some simplifications are accepted.

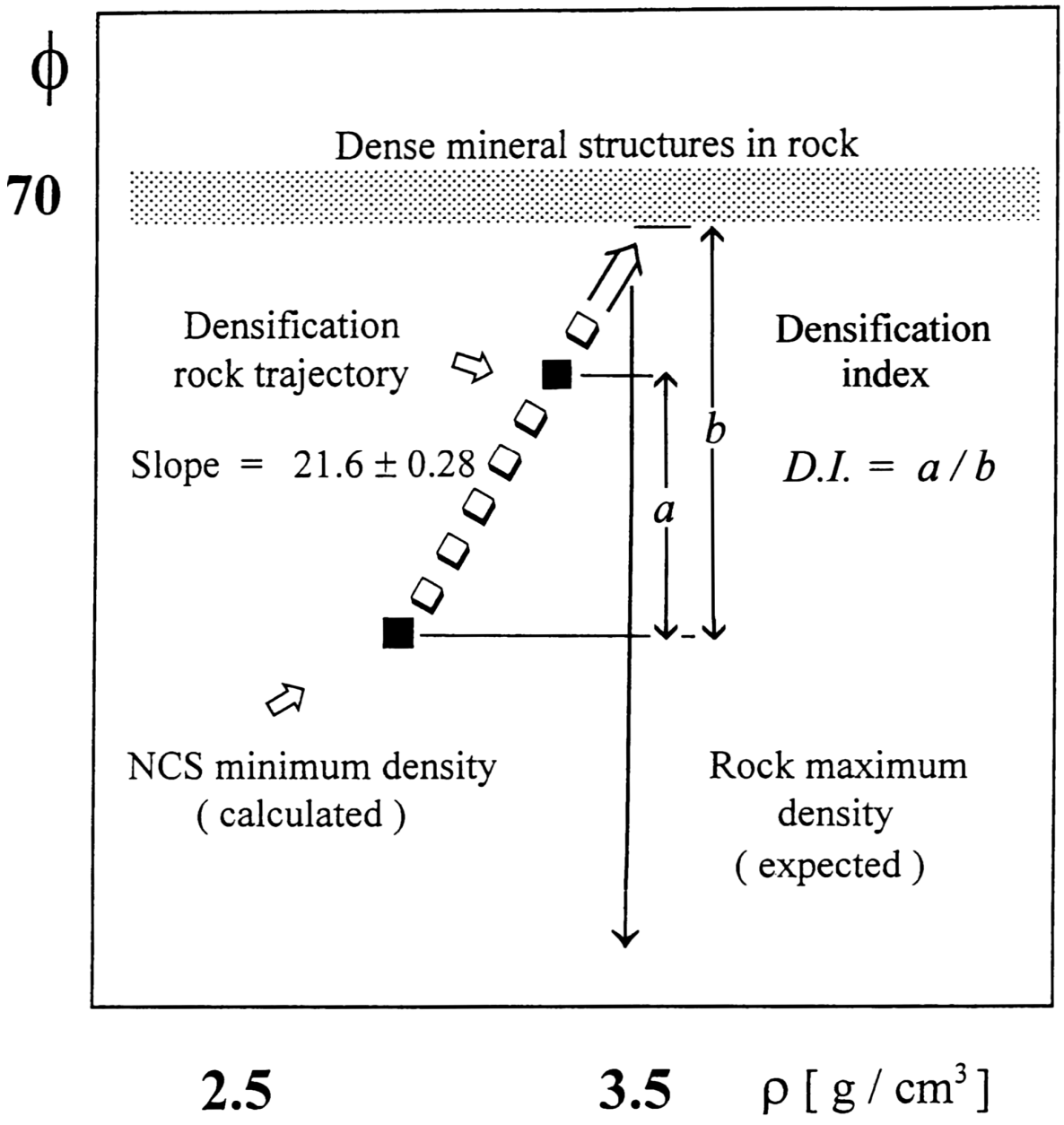

Fig. 6 Schematic presentation of rock density limits in polymineral metamorphic assemblages assessed on the basis of chemical composition and limited packing index in rocks. The dense packed pyrope - almandine garnet structures with $\phi \sim 70$ have been chosen as the *boundary limits* for crustal rocks. Packing index for eclogitic and granulitic rocks varies within the range $\phi \sim 67$-69, having thus the *densification index* D.I. = *a/b* approaching ~ 1. The studied metapelites have densification index (D.I.) from 0.22 to 0.47 (Tab. 1.), depending on the mineral composition and metamorphic grade. For the studied metapelites the rock maximum density limit is expected to be ~ 3.2 g/cm^3 and the associated space reduction in crustal metamorphic environment is ~ 17 volume %.

In crystalline oxides the Al^{3+} ion is mostly in four-fold and six-fold coordination and consequently molar volume of Al_2O_3 changes, where volume of $^{IV}Al_2O_3$ is greater than that of $^{VI}Al_2O_3$. Okuno et al. (1996) confirms the four-fold co-ordination for Al^{3+} in natural rock glasses. Consequently, present model approach assumed that aluminum was exclusively in tetrahedral coordination and thus was constrained its molar volume. However, lack of consistency about the structural details in rock glasses still persists. It includes the effects of different fluids present, oxidation states, transition properties, thermal history, kinetics of cooling, bond angles arrangements etc.

Density of a particular oxide in free state and bounded in glass is different in various compositions range. The molar volume of FeO is relatively poorly constrained but has a significant contribution to the glass density. Using the derived value of 7.16 gives high computed ρ_{NCS} value of 5.00 g/cm^3 for fayalite glass in comparison with 4.326 of Holland and Powell (1998). As the fayalite has binary nature (2 FeO.SiO_2) and V_m^{SiO2} is good constrained, the molar volume of FeO to fit the fayalite glass density has been calculated to be 10.35. This value gives satisfactory comparison data between measured and calculated density data for the fused metapelitic rock glasses (Tab. 1, Fig. 1). Thus the density calculation has been found useful for many purposes and gives interpretation data for wide range of igneous and metamorphic rocks glasses.

Density contrast is well seen in some metamorphic zones, where low grade side is similar in bulk composition with the high grade one, but the rock density on the higher grade side is significantly higher. The polyphase metamorphic assemblages are thus capable to reflect better the changing p-T conditions than e.g. quarzites, carbonates and the other quasi monomineral rocks, while higher metamorphic grade contributes to the higher rock density. Calculated densities of. e.g. basic igneous rocks, amphibolites and eclogites give small differences in normative density D_C^F, but the measured densities are significantly different as the result of p-T conditions of their formation. In igneous rock series the correlation between rock density and magmatic differentiation has long been recognised (Thorton and Tutle, 1960) and this relation may be still useful to express diverse intrusive conditions or simple magmatic source subjected to differentiation. Most of the density determinations referred to quenched glasses and their density range from ca. 2.3 g/cm^3 for granitoidic compositions to about 2.8 g/cm^3 for basaltic rocks (Carmichael, 1979). For granitoidic rocks the crystallization contraction values correspond to approximately 6-14 % volume change (see e.g. Dyda, 1999).

The calculated ρ_{NCS} and ϕ_{NCS} place the particular rock sample within the ρ versus ϕ co-ordinates. Higher density or packing index need not represent the higher densification index for the sample, as well as higher ρ or ϕ alone, does not represent higher metamorphic temperatures or pressures to which the rock sample might have been exposed (see e.g. I1, I2, I3 and P1, P2, P3 in Fig. 5). However, the presented densification index in Fig. 6 is a good comparison tool and metamorphic grade indicator expressing density and volume change limits in recrystallizing rocks.

CONCLUSION

Densities of rock glasses (ρ_{NCS}) can be calculated on the basis of their chemical composition and molar volume (V_m) of the rock forming oxides. The calculated ρ_{NCS} and measured ρ_{GLASS} density data have a high correlation (r = 0.97) in the metapelitic rock composition. The calculated ρ_{NCS} is the minimum density reference unit with the lowest packing index (ϕ) for the given composition.

The *densification trajectories* of minerals and rocks presented within the ρ versus ϕ co-ordinates give the specific slope of $a = 21.6 \pm 0.28$. This slope has almost the same value if describing phase transition, melting phenomena and metamorphic reaction extent.

Using the modelled relations among the rock bulk chemical composition, rock density and packing index, the *rock density limits* can be estimated and *densification index* (D.I.) defined.

The assessment of volume changes and density limits play a primary importance in the Earth crust and mantle, in tectonic environment of the subduction zones where density differences determine the dynamics of many geological processes.

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Appendix I.

Chemical composition of the studied rocks expressed in 160 oxygen Barth rock unit cell*.

2.	$K_{3.650}Na_{3.892}Ca_{0.820}Mg_{3.293}Mn_{0.104}Fe^{2+}_{2.547}Fe^{3+}_{2.133}Al_{16.087}Ti_{0.609}Si_{57.505}O_{160}H_{11.804}$
4.	$K_{3.332}Na_{3,332}Ca_{1,226}Mg_{3.503}Mn_{0.113}Fe^{2+}_{2.932}Fe^{3+}_{2.881}Al_{17.095}Ti_{0.659}Si_{56.643}O_{160}H_{8.831}$
5.	$K_{3.293}Na_{4.764}Ca_{0.454}Mg_{3.016}Mn_{0.097}Fe^{2+}_{2.661}Fe^{3+}_{2.527}Al_{16.309}Ti_{0.624}Si_{56.211}O_{160}H_{15.626}$
6	$K_{2.045}Na_{4.016}Ca_{1.141}Mg_{1.665}Mn_{0.110}Fe^{2+}_{0.949}Fe^{3+}_{2.692}Al_{14.821}Ti_{0.410}Si_{61.578}O_{160}H_{5.606}$
7.	$K_{3.119}Na_{5.457}Ca_{1.353}Mg_{3.670}Mn_{0.122}Fe^{2+}_{3.666}Fe^{3+}_{2.898}Al_{18.038}Ti_{0.637}Si_{54.219}O_{160}H_{11.554}$
8.	$K_{3.585}Na_{3.566}Ca_{1.099}Mg_{3.363}Mn_{0.105}Fe^{2+}_{3.103}Fe^{3+}_{2.705}Al_{18.405}Ti_{0.603}Si_{54.802}O_{160}H_{11.545}$
9.	$K_{3.834}Na_{4.792}Ca_{1.309}Mg_{3.492}Mn_{0.122}Fe^{2+}_{3.884}Fe^{3+}_{3.011}Al_{19.190}Ti_{0.694}Si_{53.540}O_{160}H_{10.206}$
10.	$K_{2.374}Na_{4.760}Ca_{1.376}Mg_{2.057}Mn_{0.081}Fe^{2+}_{0.884}Fe^{3+}_{3.340}Al_{16.801}Ti_{0.512}Si_{57.993}O_{160}H_{9.617}$
11.	$K_{2.277}Na_{4.604}Ca_{1.432}Mg_{2.136}Mn_{0.104}Fe^{2+}_{2.280}Fe^{3+}_{2.184}Al_{14.391}Ti_{0.529}Si_{61.227}O_{160}H_{4.458}$
12.	$K_{3.678}Na_{5.982}Ca_{1.770}Mg_{3.475}Mn_{0.108}Fe^{2+}_{4.676}Fe^{3+}_{1.886}Al_{20.264}Ti_{0.731}Si_{53.401}O_{160}H_{7.288}$
14.	$K_{2.979}Na_{3.871}Ca_{0.735}Mg_{3.028}Mn_{0.120}Fe^{2+}_{3.324}Fe^{3+}_{2.588}Al_{19.428}Ti_{0.5761}Si_{55.393}O_{160}H_{8.799}$
17.	$K_{2.974}Na_{4.279}Ca_{1.431}Mg_{2.913}Mn_{0.113}Fe^{2+}_{3.075}Fe^{3+}_{2.578}Al_{18.017}Ti_{0.546}Si_{55.749}O_{160}H_{10.709}$
18.	$K_{4.679}Na_{4.133}Ca_{0.580}Mg_{4.321}Mn_{0.099}Fe^{2+}_{3.075}Fe^{3+}_{2.943}Al_{19.862}Ti_{0.672}Si_{51.536}O_{160}H_{17.053}$
19.	$K_{3.003}Na_{3.490}Ca_{0.000}Mg_{2.573}Mn_{0.029}Fe^{2+}_{1.278}Fe^{3+}_{2.605}Al_{14.138}Ti_{0.432}Si_{59.302}O_{160}H_{16.561}$
KB1.	$K_{2.178}Na_{5.467}Ca_{1.801}Mg_{2.505}Mn_{0.105}Fe^{2+}_{2.320}Fe^{3+}_{2.556}Al_{19.241}Ti_{0.561}Si_{56.061}O_{160}H_{7.001}$
KB2.	$K_{2.715}Na_{4.994}Ca_{1.696}Mg_{3.132}Mn_{0.136}Fe^{2+}_{2.693}Fe^{3+}_{2.853}Al_{18.208}Ti_{0.551}Si_{56.136}O_{160}H_{7.039}$
KB3.	$K_{2.108}Na_{6.651}Ca_{2.373}Mg_{1.943}Mn_{0.098}Fe^{2+}_{1.994}Fe^{3+}_{2.406}Al_{17.492}Ti_{0.463}Si_{58.296}O_{160}H_{3.873}$
KB4.	$K_{3.388}Na_{5.570}Ca_{1.887}Mg_{3.029}Mn_{0.107}Fe^{2+}_{3.354}Fe^{3+}_{2.508}Al_{17.286}Ti_{0.625}Si_{56.969}O_{160}H_{4.519}$
KB5.	$K_{3.312}Na_{5.534}Ca_{2.012}Mg_{3.540}Mn_{0.218}Fe^{2+}_{3.857}Fe^{3+}_{3.270}Al_{21.263}Ti_{0.713}Si_{51.603}O_{160}H_{9.028}$

* Rock unit cell has been used for direct *V/Atoms*, *V/Oxygen* ratio calculations, packing index (ϕ) calculations for rocks and non crystalline solid reference units (NCS), where density (ρ), effective ion volume (V_i) and chemical composition of the substance is required.

Appendix II.

I. Glass density calculation:

Diopside $CaMgSi_2O_6$ ρ_{NCS} calculation according to formula (1): $\rho_{NCS} = \sum_{i=1}^{n} M_i X_i / \sum_{i=1}^{n} Vm_i X_i$

	W %	X_I	Vm_i			
SiO_2	55.49	0.250	26.40	ρ calculated	ρ_{NCS} =	2.86
MgO	18.61	0.250	10.21	ρ measured	ρ_{Glass} =	2.85
CaO	25.89	0.250	12.71			

Density of the anorthite glass measured is $\rho_{GLASS} = 2.69$, anorthite glass computed is $\rho_{NCS} = 2.72$.

II. Packing index (ϕ) calculation:

Phlogopite $KMg_3Si_3AlO_{10}(OH)_2$ $XY_3Z_4O_{10}(OH)_2$

$Z = 2$

$V_0 = 496.9$ (Å^3)

$\rho = 2.788$ (g/cm^3)

$\phi = V / V_o = [4\pi / 3 \sum_{i=1}^{n} (f_i r_i^3)] / V_o$

		I.R.	Ion volume
Z^{IV}	Si	0.26	0.0736
	Al^{3+}	0.39	0.2484
Y^{VI}	Al^{3+}	0.53	0.6236
	Fe^{3+}	0.53	0.6236
	Fe^{2+}	0.61	0.9507
	Mg	0.72	1.5634
	Mn	0.67	1.2598
	Ti	0.605	0.9275
X^{XII}	K	1.60	17.1572
	Na	1.32	9.6340
	Ca	1.35	10.3059
	O	1.38	11.0084
	OH	1.36	10.5367

$\phi = 2[17.1572 + 3 \times 1.5634 + 3 \times 0.00736 + 0.2484 + 10 \times 11.0084 + 2 \times 10.5367] / V_o$

$\phi = (2 \times 153.747) / 496.9 = 0.617$

Thus the 'empty space' in the crystal structure of phlogopite is ca. 38 %.
