[American Journal of Science, Vol. 301, June, 2001, P. 557–592]

# A THERMODYNAMIC MODEL FOR Fe-Mg ALUMINOUS CHLORITE USING DATA FROM PHASE EQUILIBRIUM EXPERIMENTS AND NATURAL PELITIC ASSEMBLAGES IN THE 100° to 600°C, 1 to 25 kb RANGE

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**ABSTRACT.** The purpose of this study is to derive a solid solution model for aluminous (Si < 3 a.p.f.u.) chlorites encountered in metapelites over a wide range of P-T conditions. A compilation of chlorite compositions in quartz-bearing rocks led us to propose a four-thermodynamic-component (Mg-amesite, clinochlore, daphnite, and Mg-sudoite) solid solution model that accounts for the Tschermak, Fe-Mg, and di/trioctahedral substitutions observed in nature. A new feature emerging from this compilation is the contrasting effect of temperature and pressure variations on the Al$^{IV}$ and vacancy contents in chlorites. A 3-site mixing model with symmetric Margules parameters and ideal inter-site interaction has been adopted to model these compositional changes. In contrast to previous models, the relevant thermodynamic data (Mg-amesite and daphnite standard state properties as well as $W_{AlMg}$, $W_{AlFe}$, $W\square_{Fe}$, $W\square_{Mg}$, *and* $W\square_{Al}$ *on M1)* are calibrated with independent sets of published experiments conducted in the MASH and FMASH systems ($\sim$60 reversals) as well as about 200 natural data involving chlorite + quartz ± (carpholite or chloritoid) assemblages. Moreover, the constraints span a wide range of pressure and temperature conditions (100°-850°C, 0.5-20 kb), so that no extrapolation outside the calibration range is needed for P-T thermobarometric purposes. The calculated thermodynamic data are compatible with the thermodynamic data of clinochlore from Berman (1988), Mg-sudoite and Mg-carpholite data from Vidal and others (1992), Fe-chloritoid from Vidal and others (1994), and the chlorite-chloritoid Fe-Mg exchange thermometer of Vidal and others (1999). The chlorite solution model seems to be consistent also with the solid solution properties from Berman (1990) for garnet, Fuhrman and Lindsley (1988) for plagioclase, and Evans (1990) for epidote, although additional work is required to explain the large discrepancies observed between the temperatures obtained from empirical garnet-chlorite Fe-Mg exchange thermometers and the temperatures calculated in the present study.

The use of several chlorite endmembers makes the estimation of paleo-pressure and -temperature conditions possible for high-variance parageneses (> 1) which is not possible when using only one chlorite endmember (classically clinochlore). In particular, reliable pressure estimates can be made for the common chlorite-quartz-carpholite or chloritoid or garnet bearing rocks devoid of aluminosilicates, whereas such estimates are impossible when using only one chlorite endmember. In the most favorable cases, temperature conditions can be estimated from the location of the temperature-dependent equilibrium 2 clinochlore + 3 Mg-sudoite = 4 Mg-amesite + 7 quartz + 4 $H_2O$, that is from the composition of chlorite associated with quartz. Our chlorite solution model predicts that at fixed pressure and $(XMg)_{chlorite}$, the location of this equilibrium is shifted toward higher temperature when decreasing the Si, Al$^{VI}$, and vacancy contents and increasing the Al$^{IV}$ content. This result is compatible with the classical empirical thermometers based on the Al$^{IV}$ and vacancy contents in chlorite. However, the calculated effect of pressure is an increase of the Al$^{IV}$, Al$^{VI}$, and vacancy contents. This explains why the empirical chlorite thermometers (based on the Al$^{IV}$ contents in chlorite) derived from low-T samples cannot be used at high pressure conditions.

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## INTRODUCTION

Chlorite is common in a great variety of rocks and geological environments. It displays a wide range of chemical compositions that reflect its physicochemical conditions of formation. Therefore, chlorite presents an interesting potential for thermobarometric estimates.

Two approaches have been proposed to use the compositional variability of chlorite to determine the thermobarometric conditions prevailing during its formation: (1) the use of empirical calibrations based on the tetrahedral aluminium occupancy as a function of measured temperature in geothermal systems (Cathelineau and Nieva, 1985; Cathelineau, 1988; Kranidiotis and MacLean, 1987; Jowett, 1991; Hillier and Velde, 1991; among others), and (2) thermodynamic calculation of equilibrium conditions for chlorites whose composition is expressed as a linear combination of a set of endmember components of known thermodynamic properties. The mixing properties between these endmembers are either calibrated using experimental data (McPhail and others, 1990; Holland and others, 1998) obtained at high temperature ($> 500°C$) in the simplified $MgO$-$Al_2O_3$-$SiO_2$-$H_2O$ (MASH) chemical system or derived assuming ideal mixing for cations on energetically equivalent sites (Walshe and Solomon, 1981; Walshe, 1986).

Because of its simplicity, the first approach has been increasingly used in diagenetic settings in recent years. However, studies aimed at identifying the chlorite composition variations with P and T indicate that chlorite compositions are not only sensitive to conditions of metamorphism but also to bulk rock composition (Zane and Sassi, 1998). Moreover, significant variations of composition can occur among chlorites coexisting in the same hand sample or even in the same thin section. This reflects the fact that different specific assemblages drive the substitutions in different directions with changing P and T. Consequently, empirical methods based on the composition of chlorite alone cannot provide reliable P-T estimates. Furthermore, the application of such empirical thermometers is restricted to temperatures (below 300°C), rock mineralogies, and compositions at which they were calibrated. For these reasons, various equations based on different rock compositions have been proposed, but none of them gives reliable results over a wide range of physicochemical conditions of crystallization (DeCaritat and others, 1993).

The use of thermodynamics is an improvement to the empirical thermometer, since it accounts for the variations of the rock mineralogy and the potential influence of additional thermophysical parameters (that is fluid composition or redox conditions, Walshe and Solomon, 1981; Walshe, 1986). However, none of the models published to date is able to account for the composition of chlorite observed from low-grade metamorphism to its breakdown temperature conditions (about 850°C at 15 kb in MASH; Baker and Holland, 1996). The solution components used by Walshe (1986) account for the relevant substitutions observed in natural chlorite, including $FeMg_{-1}$ (FM), Tschermak (TK), and di-trioctahedral (DT) substitutions, but the thermodynamic data and activity-composition model are not constrained by the P-T-composition relations observed at $T > 400°C$ and $P > 5$ kb in either experimental systems or in nature. Conversely, thermodynamic data and solution models extracted from experiments do not account for all substitutions observed in natural chlorites. McPhail and others (1990) calculated thermodynamic properties for an Al-free trioctahedral chlorite of Mg-serpentine composition (ChlS: $Si_4(Mg)_6O_{10}(OH)_8$) and for Mg-amesite (Mg-Am:$Si_2Al_4Mg_4O_{10}(OH)_8$) which allows the extent of TK substitution with P-T conditions to be modeled in the experimental MASH system but not the extent of FM and DT substitutions observed in nature. Holland and others (1998) proposed a non-ideal activity model accounting for the compositional and possible ordering variations (reciprocal solutions) among four endmembers (Mg-Am, ChlS, clinochlore (Clin: $Si_3Al_2Mg_5O_{10}(OH)_8$), and daphnite (Daph: $Si_3Al_2Fe_5O_{10}(OH)_8$)), but the activity model assumes that the chlorite composition can be represented by the simple formula $Si_{4-x}Al_x(Mg, Fe)_{6-x}Al_xO_{10}(OH)_8$. This model only pertains to chlorites devoid of octahedral vacancies (that is, no DT substitution) for which $Al^{IV} = Al^{VI}$. However, the amount of octahedral vacancies in chlorites can be significant in rocks metamorphosed at $T < 450°C$ (see below).

The purpose of this study is to derive a solid solution model and thermodynamic data for chlorite endmember components (1) able to handle variable octahedral site occupancies independent of TK substitution and (2) that can be used to calculate the conditions of equilibrium for the most common natural chlorites encountered in metapelites, mafic, and felsic rocks over a wide range of P-T conditions, that is, chlorite with a Si content < 3 a.p.f.u. (Laird, 1988). The restriction of the model to such compositions avoids the problems related to reciprocal solutions (Holland and others, 1998). In contrast to previous models, we attempt to constrain the relevant thermodynamic data with independent sets of published experiments conducted in the MASH and FMASH systems (300°-850°C, 0.5-25 kb) as well as various natural data from rocks of different grade.

## COMPOSITIONAL VARIABILITY OF CHLORITE IN ALUMINOUS (META)PELITES

### *Relevant Chlorite Substitutions*

Three main substitutions occur in chlorite, all of which depend on the P and T conditions as well as on the rock chemistry (or, at fixed P and T conditions, on the mineralogy). The $FeMg_{-1}$ substitution (FM) extends over the whole range between Mg and Fe endmembers, the coupled Tschermak substitution (TK: $Al^{IV}Al^{VI}Si_{-1}(Mg,Fe)_{-1}$) is restricted to chlorite compositions between Clin-Daph and Am in aluminous metapelites, and the di/trioctahedral substitution (DT) corresponds to the coupled exchange of Mg and Fe for Al in the 2:1 layer (from the (Clin/Daph)-Am binary toward the sudoite (Sud: $Si_3Al_4(Mg,Fe)_2\square O_{10}(OH)_8$) component, fig. 1). To insure charge balance, three (Mg, $Fe^{2+}$) are involved for two $Al^{3+}$, leading to the formation of one vacancy ($(Mg,Fe^{2+})_3\square_{-1}Al_{-2}$).

It is difficult to derive the extent of the DT substitution from electron-microprobe analyses (EMPA), because vacancies are not a measurable quantity. Defining the proportion of vacancies is equivocal and depends on the reference used to normalize the microprobe analyses to the structural formula (Laird, 1988). In particular, the proportion of calculated vacancies depends on the amount of $Fe^{3+}$, which is also not assessed by EMPA. A second problem arises from the possible interstratification of chlorite with other sheet silicates which might also lead to erroneous structural formulae (Jiang and others, 1994). For these reasons, Jiang and others (1994) claimed that vacancies calculated from EMPA are an artifact. However, it is generally accepted that $Fe^{3+}$ in chlorite-group minerals is controlled by crystallochemical constraints rather than by $fO_2$ conditions and is never abundant (Cooper, 1972; Black, 1975; Shirozu, 1978; Dyar and others, 1992; Nelson and Guggenheim, 1993; Zane and Sassi, 1998). Moreover, octahedral contents lower than six are also observed in low temperature chlorites devoid of significant smectite or mica contamination ($K+Na+Ca < 0.05$ a.p.f.u.). In metapelites that generally have a high (Fe/Fe+Mg) ratio, the formation of chlorite is favored instead of smectites or corrensite, and there is no important interlayering of chlorites with other sheet-silicates (Ernst and others, 1970; Ahn and Peacor, 1985; Curtis and others, 1985; Leoni and others, 1998). Therefore, octahedral vacancies in chlorites should be a real feature at $T < \sim 300°C$, $P < 1$ kb (McDowell and Elders, 1980; Cathelineau and Nieva, 1985; Cathelineau, 1988; Hillier and Velde, 1991; DeCaritat and others, 1993; Leoni and others, 1998).

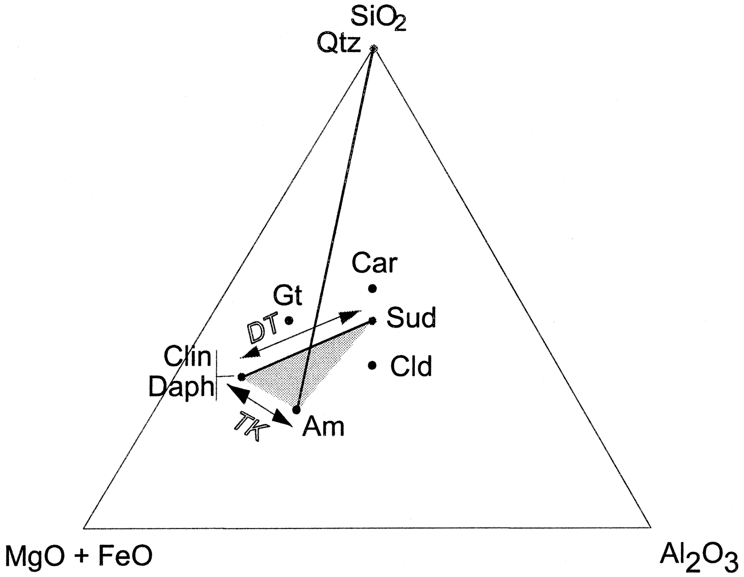

Fig. 1. Si-Al-Mg +Fe ternary for representation of the chlorite endmembers and substitutions considered in the chlorite model (for the range of composition corresponding to the gray area). TK : Tschermak substitution; DT : di/trioctahedral substitution. The chlorite + quartz stability conditions can be computed from the reaction Clin + Mg-Sud = Mg-Am + Qtz (equilibrium 4), as indicated by the intersecting tie-lines. Sud : sudoite; Clin : clinochlore; Am : amesite; Daph : daphnite; Car : carpholite; Gt : garnet; Cld : chloritoid, Qtz : quartz.

In the following, we assume that the incorporation of octahedral vacancies results only from the DT substitution. Following this assumption, the number of vacancies (□) is proportional to the difference between octahedral and tetrahedral aluminum obtained from the structural formula calculated on a 14 anhydrous oxygen basis, assuming all iron to be divalent (□ = $(Al^{VI}\text{-}Al^{IV})/2$). Any significant difference between □ and $(Al^{VI}\text{-}Al^{IV})/2$ is considered to be indicative of the presence of $Fe^{3+}$ or contamination. Such analyses were not considered in the present study (see below).

### *Influence of P-T Conditions on the Extent of Tschermak and Di/trioctahedral Substitutions*

Above ~300°C, the proportion of octahedral vacancies in low pressure environments (< 1 kb) is predicted to be 0 (Cathelineau and Nieva, 1985). However, Leoni and others (1998) showed that vacancies are still present at temperatures above 300°C in chlorites from pelites metamorphosed at higher pressure conditions. The competing effect between temperature and pressure upon the proportion of vacancies in chlorites is depicted in figure 2, which shows the molar fractions of (Clin + Daph), Am and Sud (XClin + XDaph + XAm + XSud =1, no negative Xi) in chlorites occurring with quartz ± carpholite or chloritoid at various P-T conditions (see app.). All the chlorite analyses used to construct figure 2 have a (Cr +Ca + Na + K) content < 0.07 a.p.f.u.. At low pressure, the molar fraction of sudoite (XSud = □) is effectively negligible at T above 300°C. It increases rapidly in the 300° to 400°C range, with an increase of pressure from < 1 to 3-7 kb. At high pressure conditions, XSud also decreases with temperature, but it is negligible (XSud < 0.05) at higher temperature (475°C at 10 kb or 550°C at 15 kb). Therefore, the □ = f(T) equation derived by Cathelineau and Nieva (1985) from low-temperature samples (dashed line in fig. 2) is shifted to higher temperature in the case of higher-pressure chlorite samples from chloritoid- or carpholite-bearing rocks.

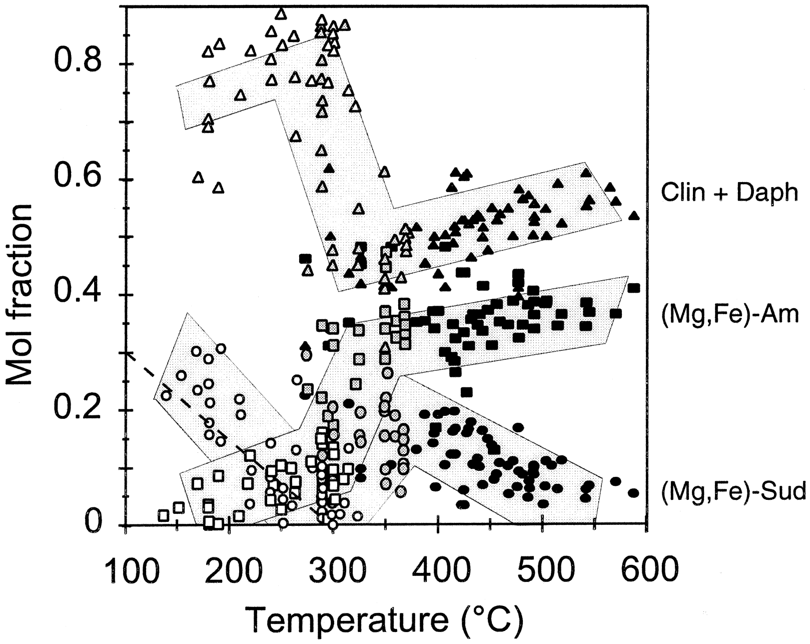

Fig. 2. Molar fractions of (Fe,Mg)-sudoite (circles), (Fe,Mg)-amesite (squares), and (clinochlore + daphnite) (triangles) in chlorites formed in quartz-bearing rocks at $P < 2$kb, $T < 350$°C (white symbols), $2 < P < 7$ kb, $250 < T < 375$°C (gray symbols) $9 < P < 16$ kb, $350 < T < 575$°C (black symbols) as a function of temperature. The composition and original temperatures are listed in the appendix. The dashed line indicates the empirical $\square = f(T)$ relation proposed by Cathelineau and Nieva (1985).

Figure 2 also shows that large variations in the clinochlore + daphnite (XClin + XDaph) and amesite (XAm) molar fractions are associated with P and T variations. At pressure below 1 kb, $0 < \text{XAm} < 0.15$ and $0.7 < \text{XClin} + \text{XDaph} < 0.85$, whereas at pressure above 10 kb, $0.3 < \text{XAm} < 0.4$ and $0.45 < \text{XClin} + \text{XDaph} < 0.6$. In both pressure domains, XClin + XDaph and XAm gently increase with increasing temperature. These trends correspond to a decrease in Si, $\text{Al}^{\text{VI}}$, and $\square$ and an increase in $\text{Al}^{\text{IV}}$ and (Fe + Mg) with increasing temperature. The pressure effects correspond to a Si and (Fe + Mg) decrease and an increase of $\text{Al}^{\text{IV}}$, $\text{Al}^{\text{VI}}$, and $\square$. Figure 2 also indicates that XAm, XSud, and (XClin + XDaph) = f(T) empirical relations (or similar relations based on the corresponding Si, $\text{Al}^{\text{VI}}$, and $\square$ content) calibrated from low-P samples cannot be used at P above 3 to 4 kb. In contrast, the chlorite thermodynamic model is expected to account for the observed XAm, XSud, and (XClin + XDaph) = f(P,T) trends.

## CHLORITE SOLUTION MODEL

At least four thermodynamic endmembers are required to model the TK, FM, and DT chlorite solid solutions. Since the present study focuses on chlorite with $\text{Si} < 3$ a.p.f.u., chlorite compositions are approximated within the system clinochlore, daphnite, Mg-amesite, Mg-sudoite. Two groups of tetrahedral sites ($(\text{T1})_2$ and $(\text{T2})_2$) and two groups of octahedral sites (M1,M4 and $(\text{M2})_2$, $(\text{M3})_2$) have been identified in chlorites (Bailey, 1988, and references therein). We distribute cations among the different sites (table 1) following Holland and others (1998), whereby octahedral Al in trioctahedral chlorite is restricted to the octahedral M1 and M4 sites with a strong preference for M4, and tetrahedral Al is restricted to T2 on which it substitutes

TABLE 1

*Thermodynamic endmember atomic site partition and method used to calculate the atomic site partition in chlorite of intermediate composition*

| | $(T1)_2$ | $(T2)_2$ | M1 | $(M2+M3)_4$ | M4 |
|---|---|---|---|---|---|
| Clin | $(Si)_2$ | Si Al | Mg | $(Mg)_4$ | Al |
| Daph | $(Si)_2$ | Si Al | Fe | $(Fe)_4$ | Al |
| Mg-Am | $(Si)_2$ | $(Al)_2$ | Al | $(Mg)_4$ | Al |
| Mg-Sud | $(Si)_2$ | Si Al | □ | $(Al)_2(Mg)_2$ | Al |
| | | | Atom site distribution | | |
| □ | 0 | 0 | $\boxed{1}$ $(Al^{VI}-Al^{IV})/2$ | 0 | 0 |
| Fe + Mg | 0 | 0 | $\boxed{3}$ $(Fe + Mg)_{tot} - (Fe + Mg)_{M2+M3}$ | $\boxed{2}$ $4 - (Al^{VI}-Al^{IV})$ | 0 |
| Mg | 0 | 0 | $\boxed{4}$ $XMg*(Fe + Mg)_{M1}$ | $\boxed{5}$ $Mg_{tot} - Mg_{M1}$ | 0 |
| Fe | 0 | 0 | $\boxed{6}$ $(1 - XMg)*(Fe + Mg)_{M1}$ | $\boxed{7}$ $Fe_{total} - Fe_{M1}$ | 0 |
| Al | 0 | $Al^{IV}$ | $\boxed{8}$ $1-(Fe+Mg+\square)_{M1}$ | $\boxed{1}$ $Al^{VI}-Al^{IV}$ | 1 |

$\boxed{1}$ to $\boxed{8}$ indicate the sequence in which the cation assignments are made, tot: total from the structural formula, $XMg = Mg_{tot}/(Mg_{tot} + Fe_{tot})$, □: vacancies.

randomly for Si. In addition, we assume that (1) vacancies in sudoite are restricted to the M1 site, (2) Fe, Mg, and Al mix randomly over the (M2 + M3) sites, and (3) there is no Mg to Fe partitioning between M1 and (M2 + M3) (that is, equal Mg/Fe proportions in these sites). The cation site distribution obtained with these assumptions is illustrated in table 1. It is emphasized that □ is calculated from the difference $(Al^{VI} - Al^{IV})$ and that $(Al)_{M1}$ is obtained from $(Fe + Mg + \square)_{M1}$. Consequently, the atomic site distribution calculation reported in table 1 can only be applied to chlorites whose composition is a linear combination of clinochlore, daphnite, amesite, and sudoite endmembers (all positive). In addition to the relations listed in table 1, the following two equations must be verified : $(Al^{VI} - Al^{IV})/2 = \square_{M1} = 6 -$ octahedral cations and $(Al)_{[M1 + M2 + M3 + M4]} = Al^{VI}$. However, analytical uncertainties may lead to some deviation from the ideal case. For this reason, chlorite compositions used as input data for the thermodynamic data extraction and application examples must meet the following criteria:

$$(Al)_{[M1+M2+M3+M4]} = Al^{VI} \pm 3 \text{ percent} \tag{1}$$

$$(Al^{VI} - Al^{IV})/2 = 6 - \text{octahedral cation sum}$$

$$\text{(from the structural formula)} \pm 15 \text{ percent} \tag{2}$$

This two criteria were used to reject analyses that cannot be expressed as a linear combination of (Fe,Mg)-amesite, (Fe,Mg)-sudoite, clinochlore, and daphnite (no negative component).

### *Formalism*

A 3-site mixing model with symmetric Margules parameters and ideal inter-site interaction has been adopted to model chemical exchange in chlorite. The formalism used in this study to calculate the endmember standard state thermodynamic properties and the mixing parameters is similar to that described by Berman and Brown (1984) and Mäder and others (1994).

For any balanced chemical reaction involving j phase components, the equilibrium condition is:

$$0 = \sum_j v_j \Delta_a G_j^{P,T} - RT \ln K \tag{3}$$

where $v_j$ is the stoichiometric reaction coefficient, $\Delta_a G^{P,T}$ is the apparent Gibbs free energy of formation (Berman, 1988), and $K$ is the equilibrium constant, which can be written as

$$K = \prod_j (a_{ideal}\gamma)_j^{v_j} \tag{4}$$

where $a_{ideal}$ is the ideal (configurational) part of the activity, and $\gamma$ is the activity coefficient accounting for non-ideal contributions.

$$(a_{ideal})_j = \prod_s \prod_m \left(\frac{ns}{r_m} Xm\right)^{r_m} \tag{5}$$

where $ns$ is the multiplicity of site $s$, $r_m$ and $Xm$ are the number and the mole fraction respectively of cation $m$ on site $s$. For the symmetric interactions assumed in this study, $\gamma_m$ is computed from:

$$n_s \cdot R \cdot T \cdot \ln \gamma_m = \sum W_{ij} \cdot X_i \cdot X_j \cdot \left[\frac{Q_m}{X_m} - 1\right] \tag{7}$$

where $W_{ij}$ is the Margules parameters, and $Q_m$ is the number of i, j subscripts equal to $m$ (0 or 1).

Eq (3) can be rearranged to compute the unknown thermodynamic parameters for known P and T conditions and known mineral compositions. Molar volumes, heat capacity, expansivity, and compressibility terms for all chlorite endmembers were either taken from the literature or estimated (table 2). Thermodynamic data for clinochlore and other minerals considered in the following were taken from the updated data set (Jan92) of Berman (1988).

The input data discussed below are insufficient to derive a unique estimate of each solution parameter for all possible interactions on each site (table 1). For this reason, $W_{AlSi}$ has been arbitrarily set to zero. $W_{FeMg}$ is also assumed to be zero which is consistent with the value (~4 kJ) predicted by the model of Davies and Navrotsky (1983) and is probably within error of zero (Holland and others, 1998). Lastly, the $W_{AlMg}$ and $W_{AlFe}$ parameters on (M2 + M3) are also set to zero because the amount of $Al_{(M2+M3)}$ is low and the possible non-ideality of the DT substitution is monitored by the □-Al, -Fe, and -Mg interactions on M1. Therefore, the remaining adjustable Margules parameters are $W_{AlMg}$, $W_{AlFe}$, $W\Box_{Fe}$, $W\Box_{Mg}$, *and* $W\Box_{Al}$ on M1, and the adjustable standard state properties are the enthalpy and third-law entropy of Mg-amesite, daphnite, and Mg-sudoite. The ideal part of the clinochlore, daphnite, Mg-amesite, and Mg-sudoite activities computed from eq (5) are:

$$a_{Daph} = 4X_{Si}^{T2} X_{Al}^{T2} X_{Fe}^{M1} (X_{Fe}^{(M2+M3)})^4$$

$$a_{Clin} = 4X_{Si}^{T2} X_{Al}^{T2} X_{Mg}^{M1} (X_{Mg}^{(M2+M3)})^4$$

$$a_{Mg-Sud} = 64X_{Si}^{T2} X_{Al}^{T2} X_{\Box}^{M1} (X_{Al}^{(M2+M3)})^2 (X_{Mg}^{(M2+M3)})^2$$

$$a_{Mg-Am} = (X_{Al}^{T2})^2 X_{Al}^{M1} (X_{Mg}^{(M2+M3)})^4$$

TABLE 2

*298K, 1 bar thermodynamic data calculated in this study (see Berman, 1988 for the format)*

|  | H°f J/mol | S° J/mol/K | V° J/bar | k0 | k1 | k2.10$^{-2}$ | k3.10$^{-3}$ | v3.10$^{5}$ K$^{-1}$ | v4.10$^{9}$ K$^{-2}$ | v1.10$^{6}$ bar$^{-1}$ | v2.10$^{8}$ bar$^{-2}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Daphnite | -7120845 | 559.4 | 21.588$^{*}$ | 1229.23$^{**}$ | -10256.5$^{**}$ | -122769$^{**}$ | 2121510$^{**}$ | 2.6451$^{***}$ | 0.00$^{***}$ | -1.819471$^{***}$ | 0.0$^{***}$ |
| Mg-Amesite | -9035900.5 | 403.2 | 20.520$^{\dagger}$ | 1144.45$^{**}$ | -8327.2$^{**}$ | -200580$^{**}$ | 2820786$^{**}$ | 2.6451$^{***}$ | 0.00$^{***}$ | -1.819471$^{***}$ | 0.0$^{***}$ |
| Mg-chloritoid | -3557301 | 132 | 6.864 | 399.52$^{**}$ | -2538.5$^{**}$ | -63616$^{**}$ | 489510$^{**}$ | 3.0000$^{\ddagger}$ | 0.00$^{\ddagger}$ | -0.675676$^{\ddagger}$ | 0.0$^{\ddagger}$ |

| Chlorites (M1) | *WH* | *WS* | *WV* |
|---|---|---|---|
| AlMg | -9400 | -30 | -0.2 |
| AlFe | 12000 | 35 | -0.5 |
| □Al | -10000 | -30 | 0.9 |
| □Fe | 2000 | -15 | 0.4 |
| □Mg | 5000 | -25 | 0.9 |
| Garnet | GE0-Calc JAN92 data base |  |  |
| Chloritoid | Ideal |  |  |
| Carpholite | Ideal |  |  |

Sources: *, estimated by Vidal and others (1999); **, estimated according to Berman and Brown (1985); ***, same as clinochlore from Berman (1988); †, Baker and Holland (1996); ‡, Comodi and others (1992)

According to the assumptions discussed above, the activity coefficients of the same endmembers are derived from the following expressions computed from eqs (6) and (7):

$$RT\ln\gamma_{Clin} = (Al - MgAl)W_{AlMg} - FeAlW_{AlFe} + (\square - \square Mg)W_{\square Mg} - \square AlW_{\square Al} - \square FeW_{\square Fe}$$

$$RT\ln\gamma_{Daph} = -MgAlW_{AlMg} + (Al - FeAl)W_{AlFe} - \square MgW_{\square Mg} - \square AlW_{\square Al} + (\square - \square Fe)W_{\square Fe}$$

$$RT\ln\gamma_{Sud} = -MgAlW_{AlMg} - FeAlW_{AlFe} + (Mg - \square Mg)W_{\square Mg} + (Al - \square Al)W_{\square Al} + (Fe - \square Fe)W_{\square Fe}$$

$$RT\ln\gamma_{Mg-Am} = (Mg - MgAl)W_{AlMg} + (Fe - FeAl)W_{AlFe} - \square MgW_{\square Mg} + (\square - \square Al)W_{\square Al} - \square FeW_{\square Fe}$$

where

$Mg$, $Al$, $Fe$ and $\square$ are molar fractions on M1.

## INPUT DATA

Table 3 lists the experimental input data as well as the corresponding equilibria used to derive the chlorite endmember and solution thermodynamic properties. The natural input data are listed in the app.

### *Experimental Constraints*

The first data available from the literature are analyses of chlorites equilibrated at fixed P-T conditions within a given mineral assemblage (Baker and Holland, 1996; Bryndzia and Scott, 1987). In such experiments, reversals were obtained by using different starting chlorite compositions, which should equilibrate with the same final composition. However, owing to the sluggish reaction rate close to equilibrium, differences in the final compositions are often observed. Experimental results were therefore interpreted as setting limits on the equilibrium composition at fixed P and T, and inequalities were derived from eq (3) through consideration of the direction from which equilibrium was approached.

Chlorites formed in the experiments of Baker and Holland (1996) are assumed to be devoid of vacancies (crystallization $T > 750°C$, see fig. 2), and the uncertainty on the compositions reported by the authors is fixed at XChl ± 0.035 on the basis of the scatter in the measured c parameter reported in their figure 4.

Chlorites crystallizing in the experiments of Bryndzia and Scott (1987) are also assumed to be devoid of vacancies, and all iron is assumed to be divalent. Moreover, Bryndzia and Scott (1987) reported that kyanite was corroded in the 6 kb pressure runs, strongly suggesting reaction of this phase. For this reason, the 6 kb results are interpreted in terms of Ky-free Chl-Qtz-Mt-$H_2O$-$O_2$ equilibrium reversals (equilibrium 12 in table 3).

Other types of experimental data used are P-T reversals of equilibria involving chlorite of known (Massonne, 1989) or unknown final composition (Staudigel and Schreyer, 1977; Chopin and Schreyer, 1983). For reasons of consistency, chlorite compositions estimated from cell parameter data are re-evaluated here using the new XRD-composition calibration obtained by Baker and Holland (1996). On the basis of the trends depicted in figure 2, the unknown amount of vacancy (not assessable from XRD) is estimated to be less than 0.1 a.p.f.u. In the case of the experiments of Chopin and Schreyer (1983) conducted at $T < 550$ °C (Car-Chl-Qtz-Ky-$H_2O$), the amount of vacancy is estimated to be less than 0.2 a.p.f.u., and it is estimated to be less than 0.1 a.p.f.u. for chlorite involved in the Cld-Chl-Ky-Co equilibrium ($550 < T < 700°C$).

TABLE 3

*Experimental constraints used for the derivation of the endmembers chlorite thermodynamic data, and nonideal solid solution parameters*

| Experimental data | Bracketed equilibria or equilibrium assemblage | Assumed uncertainties | End-members chlorite equilibria | | constrained parameters |
|---|---|---|---|---|---|
| | | $MgO-Al_2O_3-SiO_2-H_2O$ | | | |
| Baker and Holland (1996) | Chl + Opx + Fo + $H_2O$ | ± (1% + 3°C); ± 500 bars<br>Xchl ± 0.05 | 2Clin =2Fo + 2Opx +Am + $H_2O$ | (1) | H°f & S° Am,<br>$W_{AlMg}$(P,T) |
| | Chl + Sp + Co + $H_2O$ | | 3Am = 2Sp + Co + 2Clin + $4H_2O$ | (2) | |
| Massonne (1989) | Chl + Qtz = Tc + Ky + $H_2O$ | ± (1% + 3°C); ± 500 bars<br>Xchl ± 0.05 | | | $W_{AlMg}$(P,T) |
| Chopin and Schreyer (1983) | Car + Qtz = Chl + Ky + $H_2O$ | ± (1% + 3°C); ± 500 bars | 10Car + 3Am = 6Sud + 2Clin +2Ky<br>3Sud + 2Clin = 7Qtz + 4Am + $4H_2O$<br>14Ky + 4Clin+$20H_2O$ = 8Sud + Am | (3)<br>(4)<br>(5) | H°fAm, $W_{AlMg}$(P,T) |
| | Car + Dsp = Chl + Ky + $H_2O$ | ± (1% + 3°C); ± 500 bars | 8Clin + 28Dsp = 9Am + 2Sud + $2H_2O$<br>7Car + 2Am + $2H_2O$ = 5Sud + Clin<br>14Ky + 4Clin + $20H_2O$ = 8Sud + Am | (6)<br>(7)<br>(5) | H°fAm, $W_{AlMg}$(P,T) |
| | Cld = Chl + Ky + Co + $H_2O$ | | | | |
| | Cld = Prp + Co + $H_2O$ | ± (1% + 3°C); ± 500 bars | 8Clin + 14Co +$12H_2O$ = 9Am + 2Sud<br>14Ky + 4Clin+$20H_2O$ = 8Sud + Am<br>Clin + 7Cld + $5H_2O$ = 2Sud +2Am | (8)<br>(5)<br>(9) | H°f,& S°Mg-ctd,<br>$W_{AlMg}$(P,T) |
| | | | | | H°f,& S°Mg-ctd |
| Vidal and others. (1992) | Car = Sud + Qtz | ± (1% + 3°C); ± 500 bars | 2 Car = Sud + Qtz | (10) | H°f & S° Sud |
| Staudigel and Schreyer (1977) | Chl = Opx + Fo + Sp + $H_2O$ | ± (1% + 3°C); ± 500 bars | 2Clin =2Fo + 2Opx +Am + $H_2O$ | (1) | $W_{AlMg}$(P,T) |
| Jenkins and Chernosky (1986) | | | Am + Fo = Sp + Clin | (11) | |
| | | $FeO-MgO-Al_2O_3-SiO_2-H_2O$ | | | |
| Bryndzia and Scott (1987) | Chl+Mt + Qtz + $H_2O$ + $O_2$<br>+Sill or Ky ± Tc | ± 10 °C ; ± 200 bars<br>buffered $fO_2$ ± 0.5 | 4Clin + 6Dph + $5O_2$ =<br>5Am + 10 Mt + 20Qtz + 20 $H_2O$ | (12) | H°f Daph, $W_{AlFe}$(P,T) |
| Saccocia and Seyfried (1994) | Chl + Ab+Pg +Qtz + 3.2wt%<br>NaCl aqueous fluid | ± 10 °C;<br>Log($aFe^{2+}/aMg^{2+}$) ± 0.2 | $20Fe^{2+}$ + 6Ab + 2Qtz + 5Am + $2H_2O$ =<br>4Daph + 6Pg + 20 $Mg^{2+}$<br>$5Fe^{2+}$ + Clin = $5Mg^{2+}$ + Daph | (13)<br>(14) | H°f Daph, $W_{AlFe}$(P,T) |

The third type of experimental constraints are solubility equilibria investigated by Saccocia and Seyfried (1994) for the assemblage Chl-Ab-Pg-Qtz in 3.2 wt percent NaCl fluids as a function of chlorite composition from 300° to 400°C, 500 bars. Sverjensky and others (1991) claimed that a –1626 cal/mol correction to the ΔG°*f* and ΔH°*f* of Na-silicate in the Berman (1988) data base is required to obtain consistency with the Ab-Pg-Qtz solubility data of Montoya and Hemley (1975). However, the magnitude of this correction is uncertain, and Saccocia and Seyfried (1994) proposed a $-817$ cal/mol adjustment. In view of these remaining uncertainties, Saccocia and Seyfried (1994) solubility data were used to constrain the $aMg^{2+}/aFe^{2+}$ dependency as a function of chlorite composition and temperature of the $Na^+$-free equilibria only. Eqs (13) and (14) (table 3) were used for the "High-Mg chamosite" chlorite composition whereas equilibrium (14) was used only for the "Low-Fe clinochlore" composition. In effect, the amount of amesite component in "Low-Fe clinochlore" is too small to calculate a reliable Mg-amesite activity.

### *Natural data*

About 200 analyses of chlorite involved in various parageneses were used as natural constraints. The on-site molar fractions of atoms (see table 1 for the calculation procedure) are listed in the app., but complete analyses are available from the authors upon request. Part of the natural data listed in the appendix comes from the literature, and when samples were available, new analyses were performed. These data were selected:

1. for the mineralogical assemblages or geological context that allows independent P-T estimates (listed in app.).
2. for the textural and chemical evidence of equilibrium among the relevant minerals. In particular, literature data were selected for the criteria used to distinguish "primary" from "secondary" chlorites. Classical micro-structural criteria are generally sufficient to identify "peak-temperature" from "retrograde" chlorites (Vidal and others, 1999), and when different chlorite generations appeared to coexist in the same thin section, we used the analyses of the peak temperature assemblages, as explicitly described by the authors. The analyses from carpholite-bearing samples of Bousquet (1998) and Agard (1999) and from chloritoid-samples of Vidal and others (1999), as well as those performed in this study, are representative of a population of at least three analyses in the same part of the thin section. Analyzed chlorites and coexisting minerals are in contact and do not exhibit reaction features. If mineral zoning was evidenced, we considered the rim analyses only.
3. in order to cover a wide range of P-T conditions (from diagenetic environment to 600°C, 2-25 kb).
4. for their range in mineralogy. We considered only natural examples in which quartz was present, in order to constrain the thermodynamic model so that the Chl + Qtz assemblage could be used later as a temperature indicator (based on the location of the temperature-dependent equilibrium (4), table 3).

Of the ~300 analyses initially collected, 10 percent were not used because of the insufficient level of confidence concerning the P, T estimates. We then rejected EMPA analyses showing an oxygen summation lower than 84 wt percent or higher than 91 wt percent as well as those showing more than 0.5 wt percent ($Na_2O + K_2O + CaO$). The remaining analyses were screened using the constraints (1) and (2) mentioned above.

## CALCULATION PROCEDURE

The endmember standard state properties and the Margules parameters were calculated for fixed volumes, Cp(T) and V(P,T) functions (table 2). Linear programming (Berman and others, 1986) was used to solve inequalities derived from eq (1) for each set of constraints through consideration of the direction from which equilibrium was approached in experiments and consideration of the P, T, and mineral composition uncertainties for natural data (McMullin and others, 1991). Since the input constraints are of different nature and have different levels of reliability, the unknown parameters were calculated step-by-step, as indicated below. This step-by-step calculation insures that maximal weight is put on the first set of constraints with the highest level of reliability and minimal weight on the last set of data. In other words, the thermodynamic data were calculated to be compatible with all individual constraints of the first set of data (experimental phase equilibria in MASH constraining the Mg-amesite properties and $W_{AlMg}$) and kept unchanged for the calculation of the other unknowns.

### *Mg-amesite Standard State Properties and WAlMg (P,T)*

The Mg-amesite properties are directly tied to those of clinochlore used as input data. The clinochlore entropy from Berman (1988) is 25J/mol/K higher than the value predicted with Holland's (1989) method (configuration entropy = 11.52 J/mol/K). Therefore, the Mg-amesite third-law entropy ($S^\circ_{Mg\text{-}Am}$) is also expected to be higher than the value predicted with the Holland (1989) algorithm. It is constrained to lie between 385 (predicted value) and 410 J/mol/K (predicted value + 25 J/mol/K). The formation enthalpy of Mg-amesite ($H^\circ f_{Mg\text{-}Am}$) is constrained to be in the range of values predicted by Vieillard (1994). The $W_{AlMg}$ Margules interaction energy is also constrained to lie within a specific range of values (5-30 kJ/mol) consistent with the $W_{AlMg}$ = 21.431 kJ/mol calculated by Mäder and others (1994) for the M2 site of hornblendes (similar in sign and magnitude to values found by Aranovitch (1991) for orthopyroxene and Berman and others (1995) for clinopyroxene).

Initially $S^\circ_{Mg\text{-}Am}$ and $H^\circ f_{Mg\text{-}Am}$ were calculated with constant $W_{AlMg}$ from the Baker and Holland (1996) P-T-X data (fig. 3A and B), which are the most constraining experimental data available from the literature. Following this, the P and T dependency of $W_{AlMg}$ is calculated (for the H°f and S° determined above) in order to fit the Massonne (1989) P-T-X data obtained at lower temperatures and over a wider range of pressure conditions, as well as to fit reversals of Staudigel and Schreyer (1977) and Jenkins and Chernosky (1986) (see figs. 4 and 5).

### *Sudoite, Mg-carpholite, and Chloritoid Standard State Properties*

Although they were not used in the above calculations, the Mg-carpholite thermodynamic data derived by Vidal and others (1992) are compatible with the Mg-amesite and $W_{AlMg}$ data derived above. Indeed, both equilibria Car + Qtz = Chl + Ky + $H_2O$ (fig. 4) and Car + Dsp = Chl + Ky + $H_2O$ calculated with the Mg-amesite data obtained above lie within the brackets of Chopin and Schreyer (1983). Therefore, we also used the Mg-sudoite thermodynamic data from Vidal and others (1992), which are compatible with the Mg-carpholite data and the reversal of the equilibrium (10) (table 3).

Since a large part of the natural chlorite used in the following occur in Chl-Cld-Qtz assemblages, thermodynamic data for Mg-chloritoid (not included in the TWEEQ dataset) compatible with the clinochlore, Mg-amesite, and $W_{AlMg}$ data are required. The Mg-chloritoid properties were calculated from the bracketing of the equilibria Mg-chloritoid = chlorite + corundum + kyanite + $H_2O$ (fig. 6) and Mg-chloritoid = pyrope + corundum + $H_2O$ (Chopin and Schreyer, 1983) with a $S^\circ_{Mg\text{-}Cld}$ fixed at 135 ± 5 J/mol/K. Using the Fe-Cld data from Vidal and others (1994), this is equivalent to fixing the 298K, 1 bar FeMg-1 exchange entropy to –26.7 J/K/atom (Spear and Cheney, 1989).

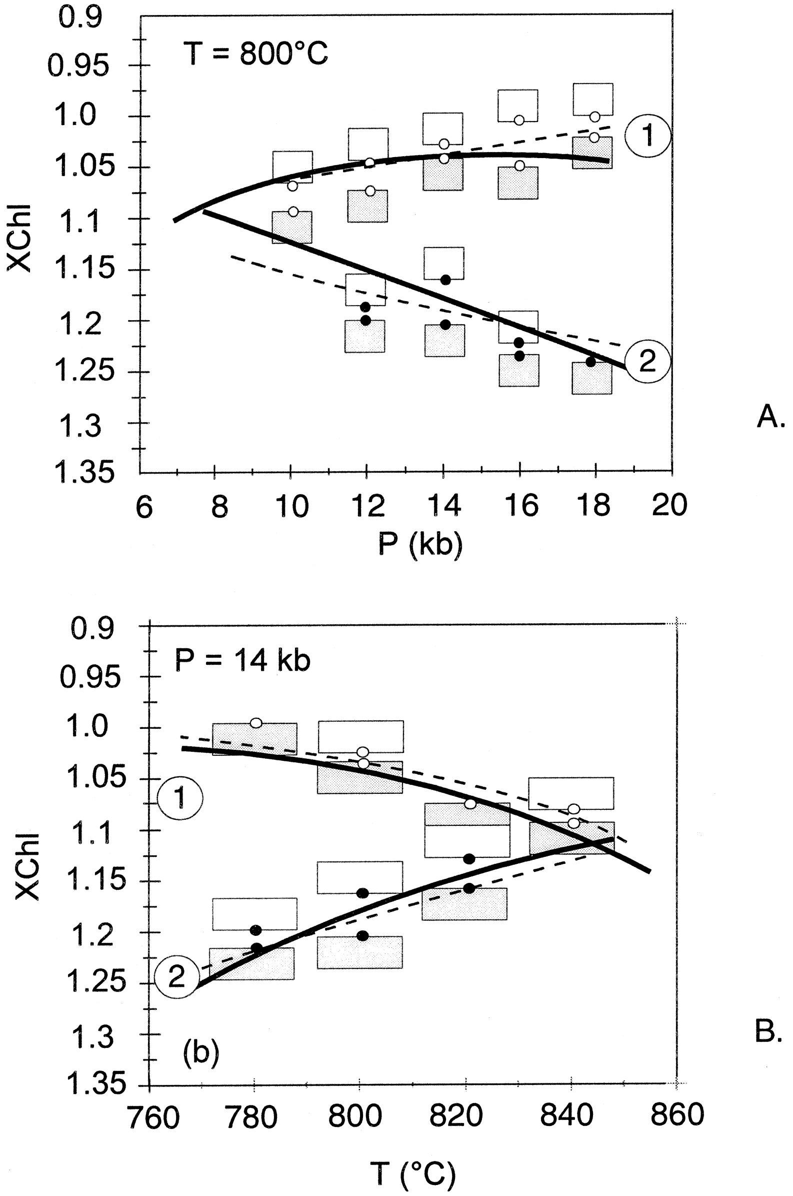

Fig. 3. Composition of chlorite (XChl = $Al^{IV}/2$) from reversal experiments of Baker and Holland (1996) for chlorite + orthopyroxene + forsterite (1) and chlorite + spinel + corundum (2). The circles show the experimental P-T conditions, and the boxes indicate the XChl, T, or P uncertainties assumed in the present study (see text). Dashed lines show the location of equilibria calculated with the chlorite solution model of Holland and others (1998), and solid lines the location of equilibria 2Clin =2Fo + 2Opx + Mg-Am + $H_2O$ (1) and 3Mg-Am = 2Sp + Co + 2Clin + $4H_2O$ (2) using the chlorite thermodynamic data and solution model proposed in the present study.

### *Daphnite Standard State Properties and* $W_{AlFe}(P,T)$

The daphnite entropy was constrained to lie within 568.7 ± 10 J/mol/K, corresponding to $S^{\circ}_{Daph} = S^{\circ}Clin - 5 \times S^{\circ}_{FeMg\text{-}1}$, with $S^{\circ}_{FeMg\text{-}1} = -26.7 \pm$J/K/atom (Spear and

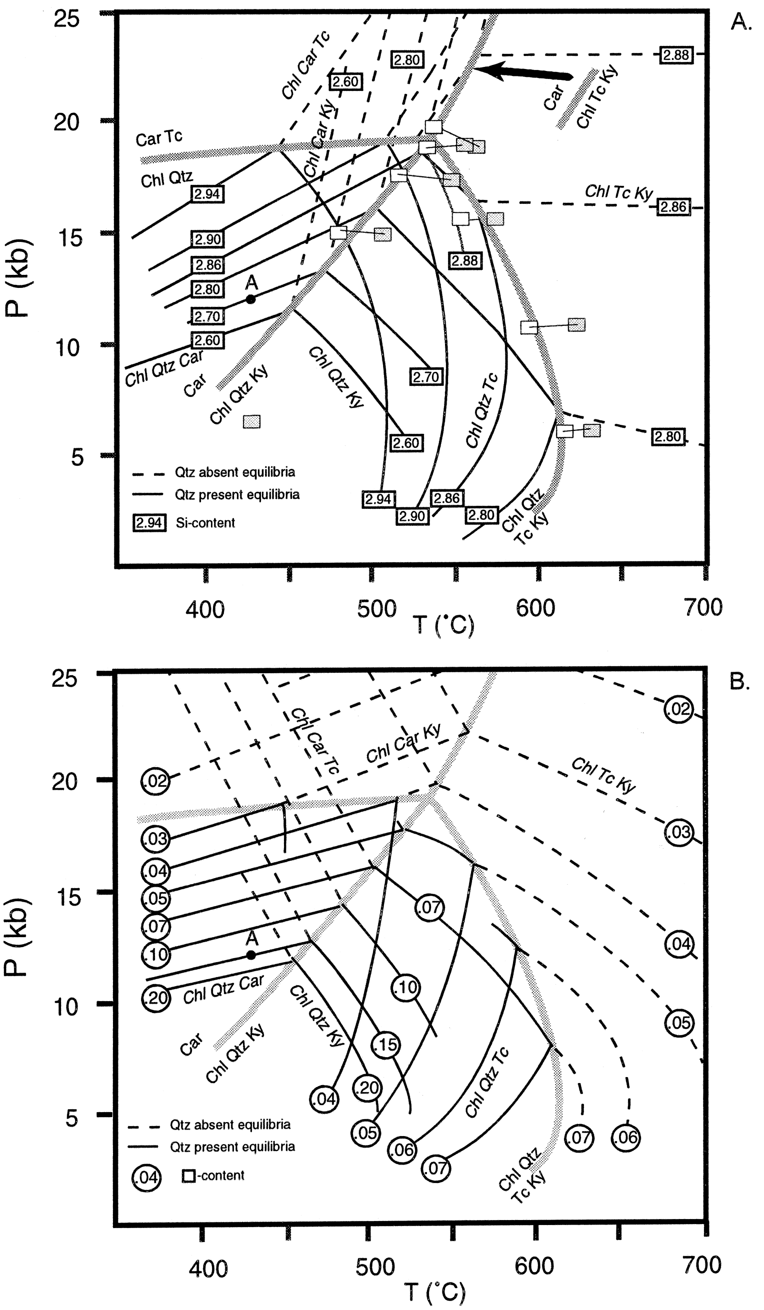

Fig. 4. Calculated chlorite composition in the $MgO$-$Al_2O_3$-$SiO_2$-$H_2O$ system in presence of carpholite (Car), talc (Tc), kyanite (Ky), and quartz (Qtz). The thin lines show the equilibrium conditions for chlorites with (A) an iso-Si content (but variable □ and Al contents) or (B) iso □-content (but variable Si and Al contents) involved in the divariant assemblages. The composition of chlorite can be calculated by combining (A) and (B). For example, the composition of chlorite coexisting with carpholite and quartz at point A is $Si_{2.7}Al_{2.6}Mg_{4.25}\square_{0.15}O_{10}(OH)_8$. At this point, the equilibria 3Sud + 2Clin = 7Qtz + 4Am + $4H_2O$, Clin + 3Car = 5Qtz + 2Am + $2H_2O$, 5Sud + Clin = 7Car + 2Am + $2H_2O$, and 2Car = Sud + Qtz intersect. The thick gray lines show the location of the univariant equilibria. The boxes in (A) show the experimental reversal from Massonne (1989) and Chopin and Schreyer (1983).

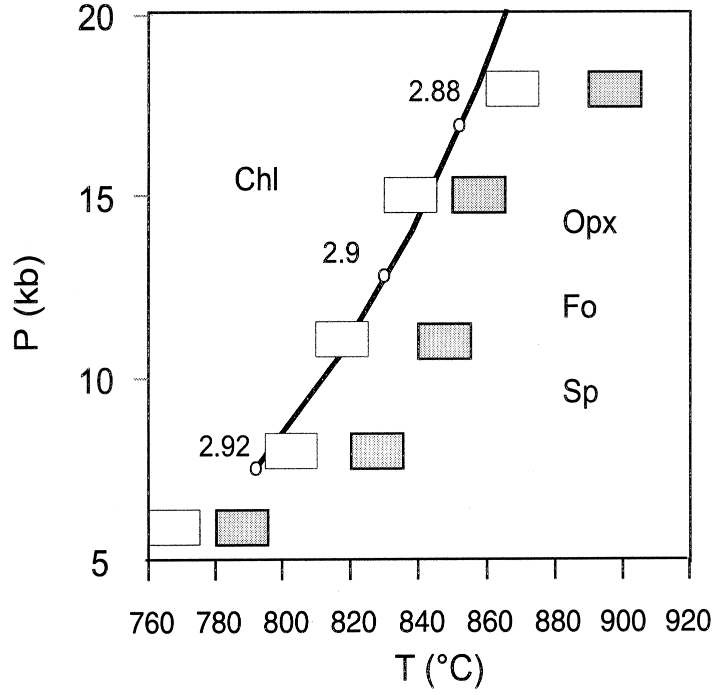

Fig. 5. Experimental bracketing of the equilibrium chlorite = orthopyroxene + forsteite + spinel + $H_2O$ after Staudigel and Schreyer (1977) and Jenkins and Chernosky (1986). The calculated location of this equilibria (assuming □ = 0) is shown by the curve, and the numbers indicate the calculated Si-content in chlorite (a.p.f.u. with a 14 oxygen basis).

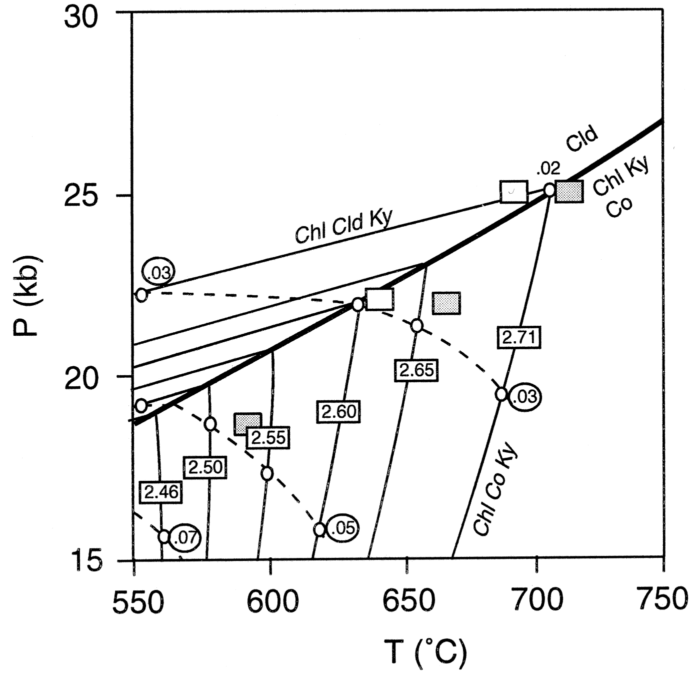

Fig. 6. Experimental bracketing of the equilibrium chloritoid = chlorite + kyanite + corundum + $H_2O$ after Chopin and Schreyer (1983). Thick line: calculated location of this equilibria. Thin lines: Si- and □- (discontinuous lines) isopleths in the divariant fields.

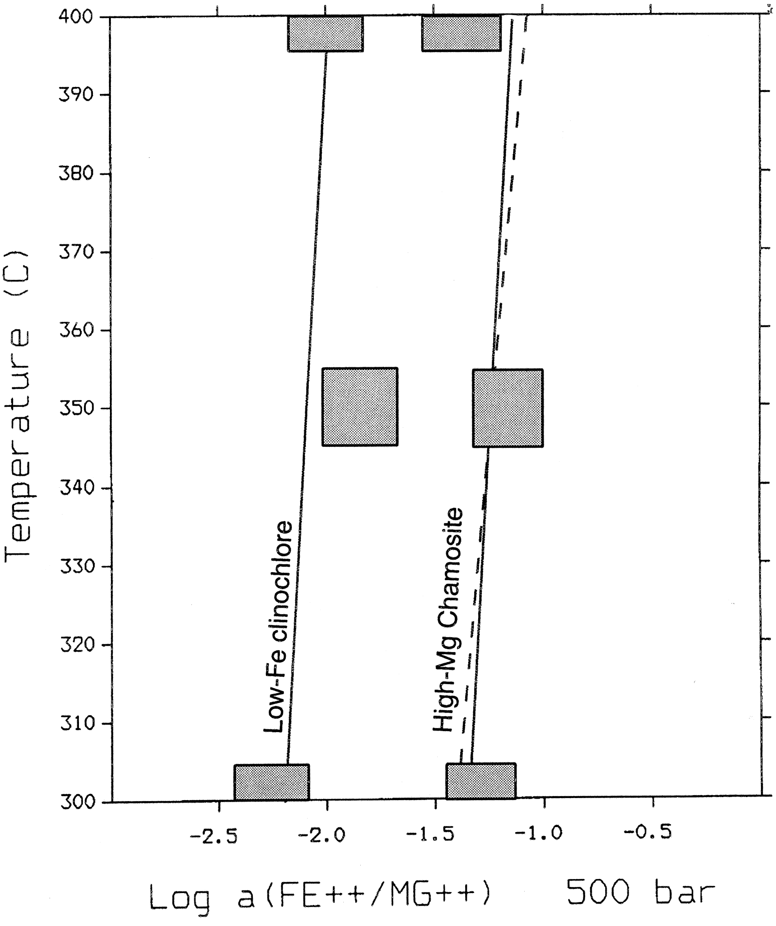

Fig. 7. The $aFe^{2+}/aMg^{2+}$ ratio for the assemblage Chl-Ab-Pg-Qtz in 3.2 wt percent NaCl fluids as a function of temperature for two chlorite compositions (Saccocia and Seyfried, 1994). The boxes correspond to the solubility measurements expanded to account for experimental uncertainties and uncertainties coming from the speciation model adopted by the authors. Lines are the calculated ratios using the chlorite data listed in table 2 and thermodynamic data for aqueous species from the TWEEQ data base. Solid lines : $5Fe^{2+}$ + Clin = $5Mg^{2+}$ + Daph; dashed line : $20Fe^{2+}$ + 6Ab + 2Qtz + 5Mg-Am + $2H_2O$ = 4Daph + 6Pg + 20 $Mg^{2+}$

Cheney, 1989). $W_{AlFe}$ was constrained to lie between −30 and −5 kJ/mol to be consistent with the $W_{AlFe} = -15.5$ kJ/mol calculated by Mäder and others (1994) for the M2 site of hornblendes (similar in sign and magnitude to the values found by Aranovitch (1991) for orthopyroxene and Berman and others (1995) for clinopyroxene). The daphnite properties and $W_{AlFe}$ parameter were calculated to locate the $aFe^{2+}/aMg^{2+}$ *versus* temperature equilibria (13) and (14) (table 3) within the experimental constraints of Saccocia and Seyfried (1994) (fig. 7). The experimental $aFe^{2+}/aMg^{2+}$ values were computed from the Fe and Mg solubility data and fluid speciation model of Saccocia and Seyfried (1994).

Attempts to calculate daphnite thermodynamic data and $W_{AlFe}$ compatible with all the experimental results reported by Bryndzia and Scott (1987) (fig. 8) were impossible, because the compositions obtained for different runs conducted at the same P-T-$fO_2$ conditions with the same starting mixtures are in some cases very different. In

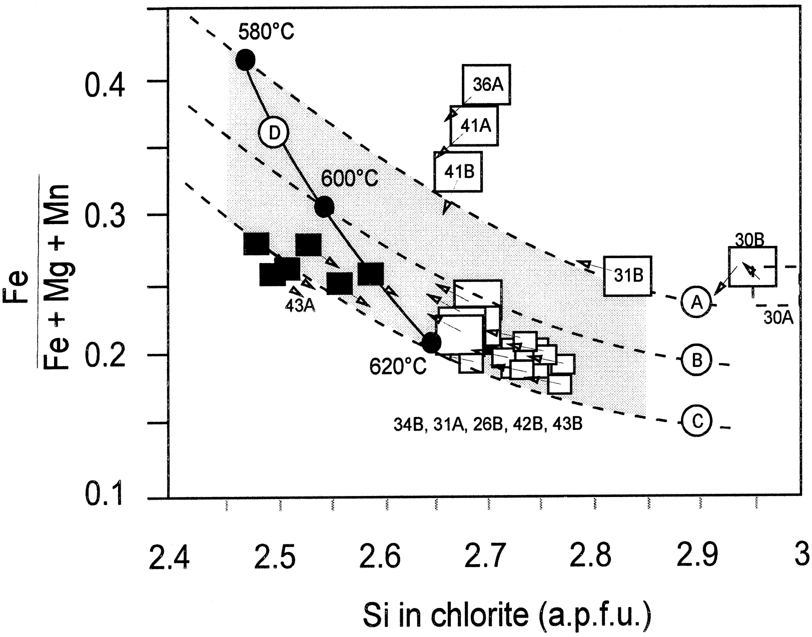

Fig. 8. Final chlorite compositions from the Bryndzia and Scott (1987) sulfidation and oxidation experiments. Small squares are from experiments 43A and B. Arrows indicate the direction in which the chlorite compositions evolved from the starting compositions. Dashed lines : calculated composition of chlorite in equilibrium with Mt + Qtz + $O_2$ + $H_2O$ at 6 kb, 580°C (A), 600°C (B), and 620°C (C). Gray area : composition of chlorite in equilibrium with Mt + Qtz + $O_2$ + $H_2O$ at 600°C, 6 kb assuming a $\log fO_2$ (buffered) ± 0.5 uncertainty. Continuous line (D) : composition of chlorite in equilibrium with Ky + Mt + Qtz + $O_2$ + $H_2O$ at 6 kb, 580° to 620°C (solid circles).

particular, large Si/Al differences are observed among chlorites equilibrated with the same assemblage at the same P-T-$fO_2$-$fS_2$ conditions (runs 30B, 31B, and 34B). This suggests that equilibrium was not achieved in all experiments. Incomplete equilibration is also indicated for most final compositions in runs 43A and B. However, since most of the final chlorites in the 600°C-6 kb runs (34B, 31A, 26B, 42B, 43B) show $2.65 < Si < 2.75$ and $0.15 < XFe < 0.25$, the Chl-Qtz-Mt- $H_2O$-$O_2$ equilibrium is believed to be closely approached for these compositions. We used the direction in which the chlorite composition evolves from the starting composition (depicted by the arrows on fig. 8) to write inequalities derived from eq 3.

The daphnite data and the P and T dependency of $W_{AlFe}$ also rely on the composition of natural chlorites with $\square < 0.025$ associated with chloritoid and quartz for which reliable P-T conditions of formation are available. The thermodynamic properties were constrained in order to locate the $(\text{Daph} + \text{Clin} + \text{Mg-Am})_{in\ chlorite}$ + (Fe-, Mg-Cld) + Qtz + $H_2O$ invariant point at the temperature equal to that estimated with the Chl-Cld exchange thermometer from Vidal and others (1999) (± 30°C) and pressure conditions in agreement with those determined originally (± 30 percent).

Chlorite-garnet natural data were not used as constraints, because textural evidence for equilibrium between chlorite and garnet is often equivocal. Moreover, garnets are generally zoned, and the determination of chlorite-garnet equilibrium compositions is uncertain. Another source of uncertainty comes from the generally low Mg-contents ($XMg < 0.1$) of garnet and therefore the significant influence of small analytical uncertainties on the magnitude of the chlorite-garnet Fe-Mg partitioning coefficient. However, selected chlorite-garnet natural data were used to check the consistency of the properties derived above with the garnet and biotite solid solution properties from Berman (1990) and McMullin and others (1991), respectively.

### $W\square_{Mg}$, $W\square_{Al}$, and $W\square_{Fe}$ Margules Parameters

The difference $W\square_{Mg} - W\square_{Al}$ was estimated so that sudoite-trioctahedral chlorite unmixing occurs in MASH at $T < 500°C$ as is suggested by the co-stability of clinochlore and sudoite in experiments (Fransolet and Schreyer, 1988; Vidal and others, 1992) and in nature (Franceschelli and others, 1989; Theye and others, 1992; Zhou and Phillips, 1994; Oberhänsli and others, 2000). Because of the lack of experimental constraints on the extent of the DT substitution with pressure and temperature, the $W\square_{Al}$, $W\square_{Mg}$, and $W\square_{Fe}$ functions were estimated from natural data obtained at $T < 500°C$. They were derived to obtain realistic temperature conditions for the equilibrium 2 Clin + 3 Mg-Sud = 4 Mg-Am + 7 Qtz + 4 $H_2O$ (4), that is the chlorite + quartz paragenesis, assuming $aH_2O = 1$. As shown in figure 2, the amount of (Mg,Fe)-amesite and -sudoite components are very low in the 275° to 350°C range at low pressure and above 500°C at high pressure. For these chlorite compositions, analytical uncertainties have a major impact on the activity of Mg-amesite and -sudoite and therefore on the equilibrium constant of (4). For this reason, we decided to use only those analyses in which X(Mg,Fe)-Am and X(Mg,Fe)-Sud $> 0.045$ (49 analyses of an initial set of 68 low-T, low-P samples, 69 of 80 Chl-Cld analyses). A first estimate of $W\square_{Al}$, $W\square_{Mg}$, and $W\square_{Fe}$ was obtained from the low-T and low-P ($< 1$ kb) samples. The final $W\square_{Al}$(P,T), $W\square_{Mg}$(P,T), and $W\square_{Fe}$(P,T) functions were adjusted to fit the following natural data:

1. fifty low-temperature ($< 450°C$) carpholite-chlorite-quartz data (Bousquet, 1998 and Agard, 1999). In the absence of thermodynamic data for Fe-carpholite (no calorimetric or experimental data), the carpholite-chlorite-quartz equilibrium conditions were calculated using Mg endmembers only. They correspond to the point where the equilibria (4), (10), Clin + 3 Car = 5 Qtz + Mg-Am + 2 $H_2O$, and 5 Mg-Sud + Clin = 7 Car + 23 Mg-Am + 2 $H_2O$ intersect.
2. sixty-nine chloritoid-chlorite-quartz data involving chlorite with $\square > 0.03$ (app.). The equilibrium conditions for this paragenesis is realized at the intersection point of 14 equilibria (involving Daph, Clin, Mg-Am, Mg-Sud, Mg-, and Fe-Cld, Qtz, and $H_2O$). Ideally, the chlorite-chloritoid Fe-Mg exchange reaction:

$$\text{Daph} + 5\ \text{Mg-Cld} = \text{Clin} + 5\ \text{Fe-Cld} \qquad (15)$$

and equilibrium (4) intersect at this point (fig. 9A). In practice, however, the equilibrium constant for (4) is much more sensitive to small compositional changes than the equilibrium constant of (15). Since the slopes of these two temperature-dependent reactions are close, small variations in the chlorite composition lead to large variations in the P-T location of the point where (4) and (15) intersect. In particular, small variations in the amount of vacancies lead to an important temperature shift of (4) but not of (15). For this reason, $W\square_{Al}$(P,T), $W\square_{Mg}$(P,T), and $W\square_{Fe}$(P,T) functions were primarily constrained in order to locate the invariant point involving Clin, Am, Daph, Fe- and Mg-Cld, Qtz, $H_2O$ at a temperature equal to that estimated with the Chl-Cld exchange thermometer from Vidal and others (1999) (± 30°C uncertainty). They were then adjusted to minimize the difference between the Fe-Mg exchange reaction and equilibrium (4) (fig. 9B and C).

3. four Sudoite-chloritoid-quartz data. We attempted to use the conditions of the Sud-Cld-Qtz equilibrium as an additional constraint for the $W\square_{Al}$(P,T),

$W\square_{Mg}$(P,T), and $W\square_{Fe}$(P,T) calibration. However, in most cases, the sudoite analyses available in the literature show a Si content > 3 a.p.f.u., whereas our activity model pertains only for chlorites with a Si content less than 3 a. p.f.u.. The few Sud-Cld analyses listed in the appendix were obtained from samples from the Lycian nappes (Oberhänsli, unpublished data) and from the Peloponnese (Trotet, unpublished data).

## RESULTS AND DISCUSSION

The calculated thermodynamic data and the chlorite solution parameters are listed in table 2. It is emphasized that the thermodynamic properties derived in this study are model-dependent and therefore are only compatible with the thermodynamic data used for their calculation as well as the atom site partition calculated as reported in table 1.

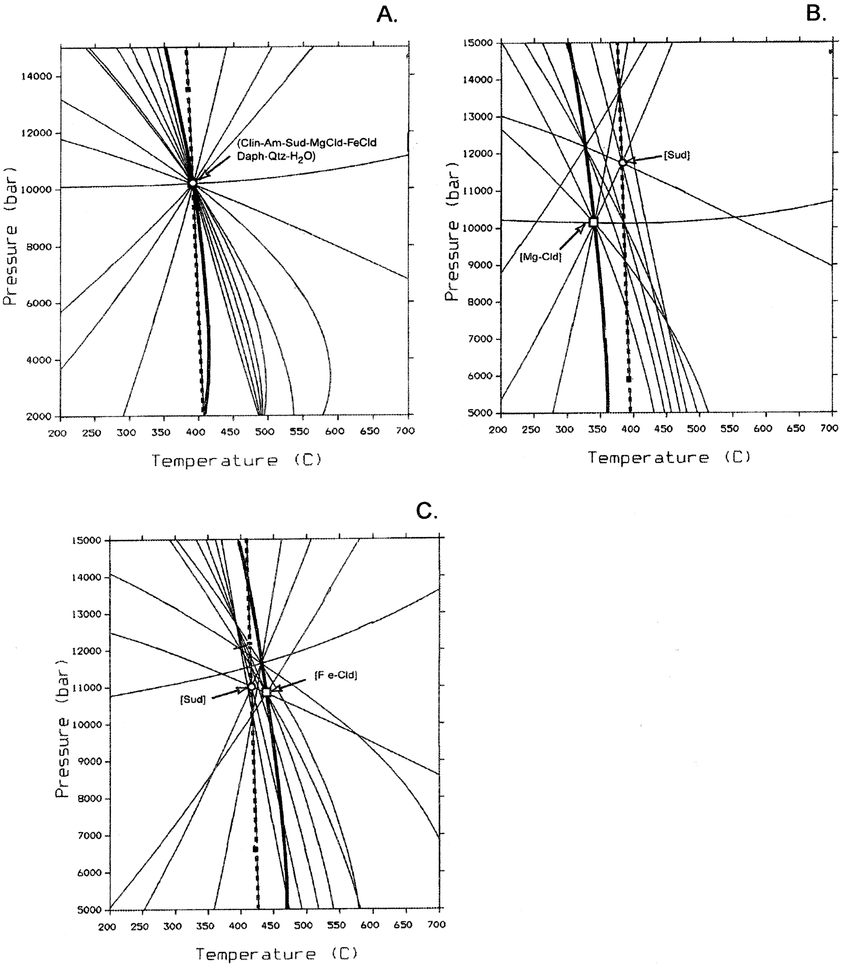

Fig. 9. Examples of multivariant equilibria calculation for the Chl-Cld-Qtz paragenesis. (A) Chl14-Cld23 from the Lycian nappes (Oberhänsli, table 4); (B) and (C): Chl68-Cld and Chl65-Cld respectively, from the Valaisan Zone (Vidal and others, 1999; table 4). Thick curves: 2Clin + 3Mg-Sud = 7Qtz + 4Mg-Am + $H_2O$ (dashed) and 5Mg-Cld + Daph = Clin + 5Fe-Cld (solid). Circle : Sudoite-absent invariant (column "II"in table 4). Square : Mg-Cld absent invariant when $T_{(4)} < T_{\mathrm{Clin\text{-}Daph\text{-}Fe,Mg\text{-}Cld}}$ or Fe-Cld absent invariant when $T_{(4)} > T_{\mathrm{Clin\text{-}Daph\text{-}Fe,Mg\text{-}Cld}}$ (see text for details).

As shown in figures 3 to 8, these data allow one to fit the experimental results obtained in the MASH and FMASH system listed in table 3 in the limit of the uncertainties and the assumptions made on the chlorite composition discussed above.

### *$MgO$-$Al_2O_3$-$SiO_2$-$H_2O$ Experimental System*

Using the thermodynamic data listed in table 2, we have recalculated the composition of chlorite involved in divariant assemblages at low temperature. For reasons of clarity, results are reported on separate parts of figure 4 (A shows the chlorite Si-content and B the □-content), but the Si-and □-content were calculated simultaneously. For example, equilibria (4), (7), (10) and Clin + 3 Car = 5 Qtz + 2 Mg-Am + 2 $H_2O$ involving a chlorite of $Si_{2.7}Al_{2.6}Mg_{4.25}\square_{0.15}O_{10}(OH)_8$ composition intersect at point A, located at 431°C, 11.9 kb on figure 4A and B. The Si-content isopleths reported on figure 4A correspond to the lines going through all the intersection points involving a chlorite of constant Si- but variable Al-, Mg-, and □-contents, whereas the □-isopleths are lines of iso □-content but variable Si, Al-, and Mg-contents.

Our results indicate that the Si- and □-contents have opposite variations with changing P-T conditions. In the chlorite-carpholite-quartz stability field, the amount of vacancy is calculated to increase rapidly with decreasing pressure, and it is predicted to be more than 0.2 a.p.f.u. below 10 kb. Although this amount may seem large, it does correspond to amounts inferred from natural Fe-Mg chlorites associated with carpholite (Bousquet, 1998; Agard, 1999, see app.). The predicted low Si-contents at these conditions also correspond to what is observed in nature.

At higher temperature, a slight increase in the content of vacancies and a decrease in Si with increasing temperature are predicted for the Chl-Qtz-Tc paragenesis, whereas the opposite is predicted for the Chl-Qtz-Ky paragenesis. It is noteworthy that below 500°C, the composition of chlorite coexisting with Tc and Qtz (in the absence of Ky) should be close to that of pure clinochlore. The chlorite compositions calculated for this assemblage are in agreement with those observed in nature by Moine and others (1982) ($2.86 < Si < 3$; $0.01 < \square < 0.05$ for $0.88 < XMg < 0.95$ at ~475°C, 1 kb) and Schreyer and others (1982) (Si = 3.04, □ = 0.015 for XMg = 0.99 at ~400°C).

At still higher temperature, the amount of vacancy in chlorite is low, and it has no influence on the location of the equilibria studied by Baker and Holland (1996), Staudigel and Schreyer (1977), Jenkins and Chernosky (1986), and Bryndzia and Scott (1987). This justifies *a posteriori* the assumptions made for the calculation of the amesite thermodynamic data and the $W_{AlMg}$ interaction parameter, that is that chlorites are devoid of vacancies in these experiments.

### *$MgO$-$FeO$-$Al_2O_3$-$SiO_2$-$H_2O$ experimental system*

We have reported on figure 7 the predicted and experimental $aFe^{2+}/aMg^{2+}$ ratio in 3.2 wt percent NaCl solution equilibrated with the two chlorite compositions used by Saccocia and Seyfried (1994). The good agreement between predicted and experimental values indicates that the relative thermodynamic properties of daphnite, Mg-amesite, and clinochlore as well as the mixing properties between these endmembers are consistent with the solubility data. In particular, the aqueous Fe/Mg concentration ratio of NaCl solutions coexisting with chlorite is predicted to increase with temperature and mole fraction of daphnite, which is consistent with the experimental results.

Figure 8 shows the final chlorite compositions analyzed by Bryndzia and Scott (1987) and the compositions calculated for chlorite in equilibrium at 6 kb with the Mt-Qtz-$O_2$-$H_2O$ (dashed lines for T =580°, 600°, and 620°C) and Ky-Mt-Qtz-$O_2$-$H_2O$ (points) assemblages. Figure 8 also shows that our thermodynamic data are consistent with all the experimental results except run 30A and their associated uncertainties (T ± 10°C, P ± 200 bars, $\log fO_2$ (buffered) ± 0.5, Si(Chl) ± 0.05 a.p.f.u., XFe ± 0.025). Runs 41A, 36, and 30 lie outside the compositional area calculated for the

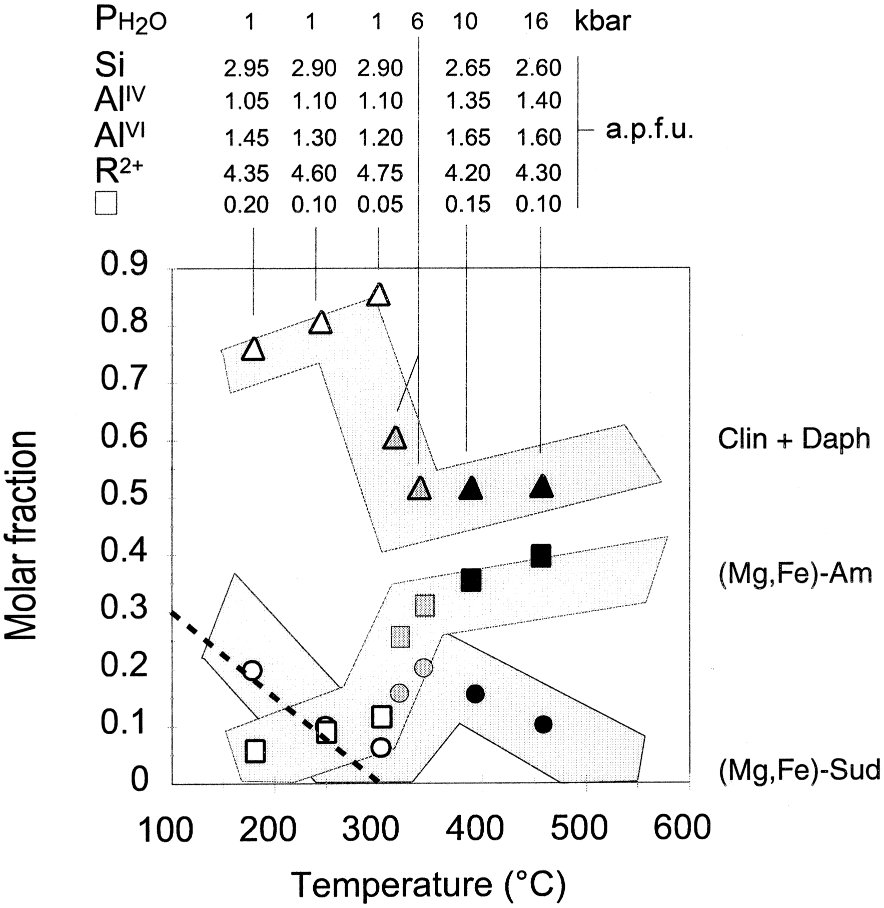

Fig. 10. Calculated molar fractions of (Fe,Mg)-sudoite (circles), -amesite (squares), and (clinochlore + daphnite) (triangles) in chlorites of fixed XMg = 0.5 equilibrated with quartz and $H_2O$ (eq 4). Dashed line : empirical □ = f(T) relation proposed by Cathelineau and Nieva (1985).

Chl-Mt-Qtz-$O_2$-$H_2O$ equilibrium (in gray on fig. 8), but the direction in which the chlorite composition evolves from the starting composition (indicated by the arrows) is compatible with the approach toward equilibrium, that is toward the calculated discontinuous lines and gray area.

### *Natural data*

In the following, we compare the new P-T estimates obtained with the chlorite model presented above with the reference values for the calibrant samples (app.). Since the P-T calculation method is paragenesis-dependent, we discussed the reliability of our estimates for each set of calibrant samples independently. However, the first validity test consists of comparing the compositional trend predicted with the model for chlorite + quartz assemblages with that evidenced in figure 2. We have calculated the clinochlore + daphnite, (Fe,Mg)-amesite and -sudoite molar proportions in chlorites of fixed XMg = 0.5 for various temperature and pressure conditions. Results are reported on figure 10 with the corresponding chlorite structural formulae and equilibrium pressure conditions. They show that the equilibrium compositions of chlorite associated with quartz and their evolution with changing temperature and pressure are in good agreement with those observed in nature. In particular, the solid-solution model accounts for the decrease in Si, $Al^{VI}$, and □ and the increase in $Al^{IV}$ and (Fe + Mg) with increasing temperature and to the decrease of Si, (Fe + Mg) and increase of $Al^{IV}$, $Al^{VI}$, and □ with increasing pressure. The chlorite model is therefore at least qualitatively consistent with the observations of McDowell and Elders (1980), Cathelineau and Nieva (1985), Cathelineau (1988), Hillier and Velde (1991), DeCaritat and others (1993), and Leoni and others (1998). It confirms that octahedral vacancies are a real feature at $T < \sim 300°C$, $P < 1$ kb which contributes to stabilize chlorite at low-T conditions. This indicates that octahedral vacancies should not be considered as an artifact resulting from incorrect normalization or contamination by other sheet silicates, as suggested by Jiang and others (1994).

A more detailed and quantitative discussion considering the additional role of XMg is done in the following by considering each set of data individually. The new P-T estimates obtained for each sample used in the calibration are listed in the app..

*Chl-Cld-Qtz assemblages.*—Three kinds of P-T estimates are reported in the app.. The first column lists the temperature location of equilibrium (4) at the pressure determined by the equilibrium Mg-Sud + Daph + Mg-Am = Fe-Cld + Clin + $H_2O$ when $T_{(4)} < T_{(15)}$ or Mg-Am + Qtz = Mg-Cld + Clin + $H_2O$ when $T_{(4)} > T_{(15)}$ (circles on fig. 9A and B). The second column lists the P-T conditions of the sudoite-absent invariant point where Mg-Am, Clin, Daph, Fe- and Mg-Cld, Qtz, and $H_2O$ coexist (squares on fig. 9A, B, and C), and the third column gives the temperature estimated with the LnKd (= $(Fe/Mg)^{Cld}/(Fe/Mg)^{Chl}$) = f(T) equation from Vidal and others (1999).

The chlorite thermodynamic properties calculated above allow one to reproduce the original P-T estimates (column "IV" in app.) within their associated uncertainties. The sudoite-absent invariants (column "II") are located at pressures that are in reasonable agreement with the original estimates and temperatures consistent with those determined with the LnKd = f(T) equation from Vidal and others (1999) (fig. 11). The temperatures estimated from the chlorite + quartz equilibrium (4) (column "I" in table 4) are less reliable, but they are generally consistent with those obtained from the location of equilibrium (15) (12 out of the 69 samples show $T_{(4)} - T_{(15)} > \pm 50°C$.

*Chl-Car-Qtz assemblages.*—Temperatures calculated for these samples rely on the location of equilibrium (4) only. However, it is emphasized that in contrast to the low-P-T Cld-Chl-Qtz samples (Dauphinois zone, app.), chlorites associated with carpholite are generally larger in size, because higher pressure conditions favor the formation of larger grains. As a consequence, the risk of obtaining contaminated chlorite analyses in the Chl-Car-Qtz samples is lower, and the reliability of the temperature estimates should be better, although the temperature conditions are similar. This is confirmed by the reasonably low scatter of the calculated temperatures which are in good agreement with the original estimates (app. and fig. 12). The pressure conditions constrained by the intersections of (4) and 2Car = $Sud_{(in\ Chl)}$ + Qtz are also in good agreement with the previous estimates.

*Low-T Chl-Qtz assemblages.*—As expected, the temperatures calculated from the location of equilibrium (4) for the low-T samples are generally lower than for the Chl-Cld and Chl-Car samples. We have reported on figure 12 the calculated temperature against the reference values (measured borehole temperatures or independent estimates). In most cases, the calculated temperatures are in reasonable agreement (±50°C) with the reference values. Since the present-day borehole temperatures may not correspond to the paleo-geotherm at which chlorite crystal-

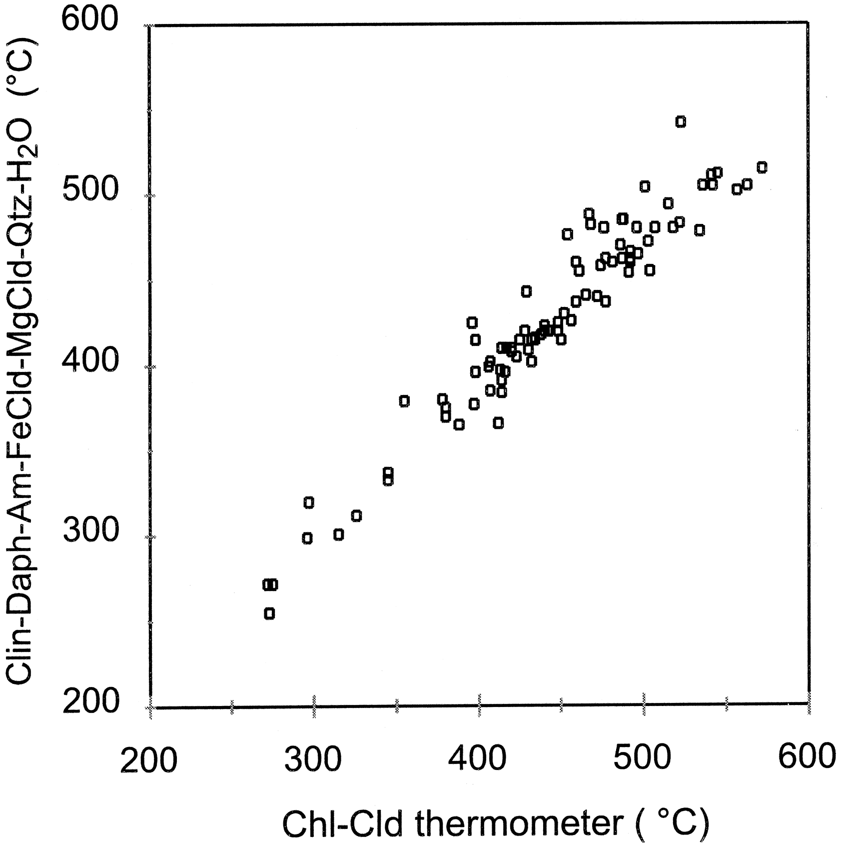

Fig. 11. Calculated equilibrium temperature for the Clin-Daph-Mg and FeCld-Qtz assemblages (circles on fig. 9, column "II" in table 4) versus temperature obtained for the same Chl-Cld pairs with the Fe-Mg Chl-Cld empirical thermometer from Vidal and others (1999) (column "III" in table 4).

lized (Hillier and Velde, 1991), a certain deviation between the calculated temperature and the reference temperature is possible. We have reported in the app. the temperatures calculated with the empirical thermometers of Cathelineau (1988) and Hillier and Velde (1991). The temperature ranges defined by these empirical thermometers and the reference temperature are depicted by horizontal bars in figure 10. Most of the temperatures determined from the location of equilibrium (4) lie within this range of temperature. They are overestimated by more than 50°C for 5 samples of the 49 listed in the app. (dashed line in fig. 12). There is no chemical argument to discard these 5 analyses. Therefore, a possible explanation for these overestimated temperatures may be the assumption that chlorite was equilibrated with a fluid with $aH_2O = 1$. Indeed, lowering the water activity leads to a shift of (4) to lower temperatures.

## APPLICATION EXAMPLES

An independent test and application example of the chlorite properties consist of recalculating the P-T conditions of Gt-Chl bearing samples not involved in the calibration, for which reliable estimates are available. Two chlorite-garnet-quartz (± epidote ± biotite ± plagioclase) samples suites from the File Lake, Manitoba (Gordon and others, 1991) and the Iberian massif (Arenas and others, 1995) were selected on the basis of their mineralogy which allow chlorite-independent P-T estimates, and for the detailed description of the textural relations and equilibrium criteria. The on-site atom partitioning calculated from the analyses are reported in table 4.

TABLE 4

*Composition of natural minerals from Gordon and others (1991) (G91) and Arenas and others (1995) (A95). The molar fraction of atom per site is calculated as indicated in table 1*

| **Chlorite-Garnet-Quartz ± Chloritoid, Plagioclase** | Sample | I | | II | III | | IV | Original estimates | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| **CHL [Si Al]$_{T2}$ [Mg Fe Al □]$_{M1}$ [Mg Fe Al]$_{(M2+M3)}$**<br>**GARN [Gros Prp Alm Sps]**<br>**PLAG [Ca Na K]**<br>**BIOT [Mg Fe Ti Al]$_{M}$ [K]$_{A}$ [OH]$_{H}$** | | T (°C) | P (kb) | T (°C) | T (°C) | P (kb) | | T (°C) | P (kb) | |
| CHL .269 .729 .259 .282 .459 .000 .478 .521 .000 | 1001 | 561$^{(1)}$ | 3(*) | 491 | 540 ± 9.9 | 1.92 ± 0.28 | 3 IR, 14 Equ. | 510-560 | 2-4 | G91 |
| GARN .037 .090 .820 .051 | | 515$^{(2)}$ | | | | | | | | |
| PLAG .251 .746 .028 | | | | | | | | | | |
| *BIOT .359 .454 .032 .147 .948 1.00* | | | | | | | | | | |
| CHL .280 .718 .261 .285 .445 .009 .476 .519 .005 | 2025 | 564$^{(1}$) | 3(*) | 490 | 541 ± 12.3 | 1.73 ± 0.43 | 3 IR, 14 Equ. | | | |
| GARN .036 .092 .839 .050 | | 530$^{(2)}$ | | | | | | | | |
| PLAG .242 .752 .006 | | | | | | | | | | |
| *BIOT .326 .455 .030 .132 .829 1.00* | | | | | | | | | | |
| CHL .260 .737 .259 .262 .476 .003 .497 .501 .001 | 2038 | 550$^{(1)}$ | 3(*) | 518 | 549 ± 4.8 | 1.96 ± 0.38 | 3 IR, 14 Equ. | | | |
| GARN .041 .095 .831 .033 | | 510$^{(2)}$ | | | | | | | | |
| PLAG .301 .696 .0028 | | | | | | | | | | |
| *BIOT .361 .425 .033 .147 .839 .972* | | | | | | | | | | |
| CHL .254 .741 .303 .237 .485 .000 .566 .442 .000 | 2040/2 | 573$^{(1)}$ | 3.2(**) | 502 | 559 ± 7.1 | 2.95 ± 0.52 | 4 IR, 29 Equ. | | | |
| GARN .063 .117 .726 .112 | | 571$^{(2)}$ | | | | | | | | |
| PLAG .449 .540 .0103 | | | | | | | | | | |
| BIOT .390 .394 .030 .135 .912 .974 | | | | | | | | | | |
| Iberian Massif | | | | | | | | | | |
| CHL .333 .667 .338 .309 .333 .019 .516 .471 .010 | 1chl1/I | 500$^{(1)}$ | 12.4(**) | 371 | 491.4 ± 7.3 | 12.33 ± 0.93 | acz = 0.26 | 470-510 | 13.5-15.5 | A95 |
| GARN .211 .046 .654 .069 | 1gt1r/I | | | | | | 3 IR, 14 Equ. | (M1) | | |
| CHL .335 .665 .353 .333 .330 .001 .512 .483 .001 | 2chl1/I | 482$^{(1)}$ | 12.1(**) | 341 | 483 ± 0.8 | 12.17 ± 0.1 | acz =0.25 | | | |
| GARN .211 .040 .654 .088 | 2gr1r/I | | | | | | 3 IR, 14 Equ | | | |
| *CHL .322 .670 .288 .354 .344 .014 .441 .541 .007* | *3chl1* | *559$^{(1)}$* | *7.4(**).* | *450* | *466 ± 56* | *13.04 ± 3.15* | acz = 0.19 | | | |
| *GARN .192 .045 .620 .124* | *3gr1r/I* | | | | | | 3 IR, 14 Equ. | | | |
| CHL .328 .669 .308 .318 .346 .027 .477 .492 .013 | 4chl1/I | 492$^{(1)}$ | 10.6(**) | 375 | 483 ± 6.4 | 10.68 ± 0.85 | acz = 0.21 | | | |
| GARN .191 .038 .593 .170 | 4gr1r/I | | | | | | 3 IR, 14 Equ | | | |
| CHL .289 .710 .314 .320 .421 .001 .499 .510 .001 | 4ch2/I | 496$^{(1)}$ | 8(**) | 433 | 498 ± 1.6 | 7.98 ± 0.34 | acz = 0.20 | | | |
| GARN .161 .045 .610 .135 | 4gr3r/I | | | | | | 3 IR, 14 Equ | | | |
| CHL .301 .698 .315 .296 .412 .001 .517 .485 .001 | 1ch2/II | 471$^{(1)}$ | 11.5(**) | 374 | 491 ± 11.9 | 12.32 ± 0.71 | 3 IR, 14 Equ | 485-530 | 10-14 | |
| GARN .099 .051 .684 .111 | 5gr1r/II | | | | | | | (M3) | | |
| PLAG .032 .968 .00 | 5pl2 | | | | | | | | | |
| CHL .312 .684 .343 .282 .374 .001 .540 .445 .001 | 2ch2/II | 492$^{(1)}$ | 11.8(**) | 393 | 504 ± 6.8 | 12.22 ± 0.41 | 3 IR, 14 Equ | | | |
| GARN .090 .062 .671 .123 | 6gr1r/II | | | | | | | | | |
| PLAG .032 .968 .00 | 5pl2 | | | | | | | | | |
| CHL .323 .674 .363 .293 .349 .001 .550 .443 .001 | 3ch2/II | 493$^{(1)}$ | 11.6(**) | 387 | 504 ± 6.5 | 12.03 ± 0.39 | 3 IR, 14 Equ | | | |
| GARN .090 .062 .671 .123 | 6gr1r/II | | | | | | | | | |
| PLAG .032 .968 .00 | 5pl2 | | | | | | | | | |
| CHL .267 .730 .255 .291 .475 .000 .469 .537 .000 | 7chl/III | 548$^{(1)}$ | 7.7(**) | 458 | 535 ± 7 | 7.31 ± 0.41 | 4 IR, 29 Equ. | 505-540 | 6.5-9 | |
| GARN .1340 .0639 .7374 .0647 | 9gt1r/II | 548$^{(2)}$ | | | | | | (M4) | | |
| PLAG .177 .812 .01 | 10pl1 | | | | | | | | | |
| BIOT .343 .477 .020 .123 .980 1.00 | 9bt2/II | | | | | | | | | |
| CHL .327 .672 .317 .291 .343 .049 .505 .462 .024 | 11ch/III | 560$^{(1)}$ | 5.15(**) | 450 | 551 ± 6.8 | 4.92 ± 0.65 | 4 IR, 29 Equ. | | | |
| GARN .1198 .0769 .7326 .0708 | 10gr1r/II | 560$^{(2)}$ | | | | | | | | |
| PLAG .268 .732 .00 | 11pl1 | | | | | | | | | |
| BIOT .333 .437 .020 .150 .960 1.00 | 9bt1/II | | | | | | | | | |

I: Gt-Chl (1) and Gt-Bt (2) exchange reactions at fixed (*) or calculated (**, Chl-Gt-Qtz-Bt or Ep invariant) pressure; II: Gt-Chl thermometer of Grambling (1990); III: TWEEQ computation of equilibria among chlorite, garnet, plagioclase and quartz and $H_2O$ in the system CaO-MgO-FeO-$K_2O$-$Al_2O_3$-$SiO_2$-$H_2O$ (1 $\sigma$ uncertainties from INTERSX); IV: clinozoisite activities (acz), number of independent reactions (IR) and number of equilibria on which the results listed in III are based.

The equilibrium conditions were calculated using the INTERSX software (included in the TWEEQ package; Berman, 1991), using the solution model and mixing properties from Berman (1990) for garnet, McMullin and others (1991) for biotite and Furhman and Lindsley (1988) for plagioclase (see Berman, 1991 for more details).

*File Lake area.*—Sample 2026-2 was excluded because $(Na + K + Mn + Ca)_{chlorite}$ 0.07, and sample 2027 because it is garnet-free. Calculation of equilibrium conditions based on water-free assemblages indicates that temperatures determined by the Gt-Chl

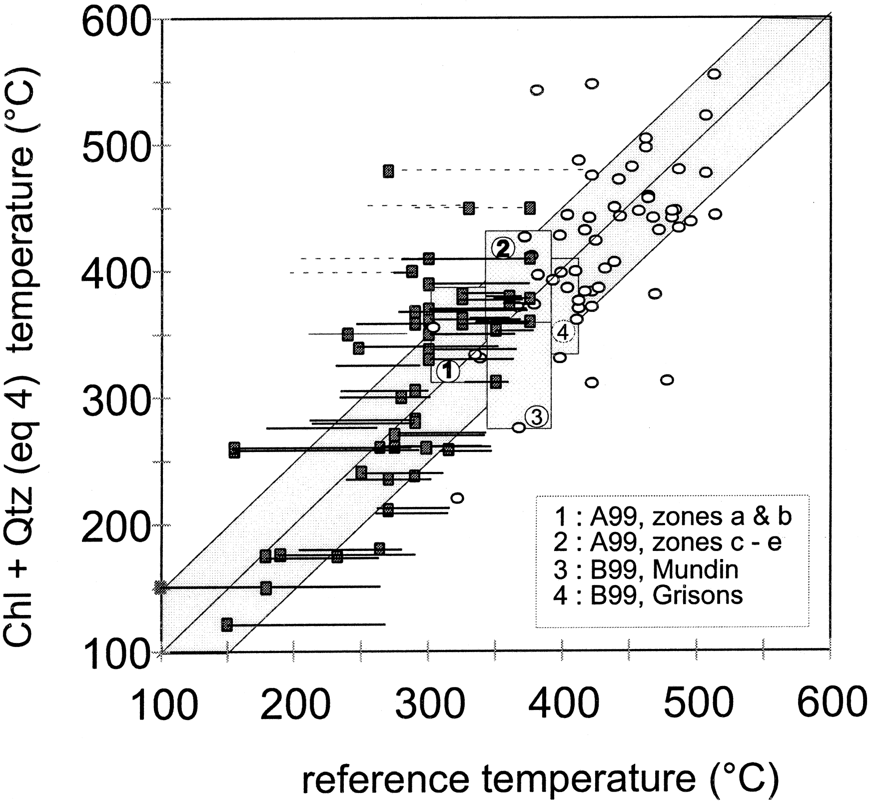

Fig. 12. $T_{(4)}$ versus original T for Car-Chl (large boxes) and low-T Chl-Qtz samples (squares) samples, or temperature calculated with the empirical thermometer from Vidal and others (1999) for Chl-Cld-Qtz samples (circles). The horizontal bars represent the temperature range determined by the original value (square), and those obtained with the empirical thermometers of Cathelineau (1988) and Hillier and Velde (1991).

Fe-Mg exchange reaction are in fair agreement with the previous estimates by Gordon and others (1991) and are consistent with the assumed increase of temperature across the Sill + Bt isograd. However, these temperatures are higher than those determined by the Gt-Bt equilibrium (+35°C for 2025, +40°C for 2038, and +45°C for 1001), and the Chl-Bt exchange reaction is located at unrealistically high pressure (fig. 13A) except for sample 2040-2 (fig. 13B). This sample is the only one for which reasonable P-T conditions with a small scatter are obtained for the $H_2O$-free Gt-Bt-Chl-Pl-Qtz assemblage (P = 3204 kb (1 $\sigma$ = 75 bar), T = 573°C (2.1)) calculated from 8 equilibria (3 independent reactions) involving Alm, Pyr, Gros, Daph, Clin, Mg-Am, Phl, Ann, An, and Qtz endmembers (fig. 13A). These results suggest that biotite is equilibrated with chlorite in samples 2040-2 only, or that the chlorite solution properties are not compatible with the biotite solution properties from McMullin (1991). On the contrary, equilibrium between chlorite, garnet, plagioclase, and water ($aH_2O = 1$) was closely achieved in all samples, and the chlorite data calibrated above are compatible with the solution properties from Berman (1990) for garnet and from Furhman and Lindsley (1988) for plagioclase. This is shown by the low scatter (7°-12°C, 0.28-0.52 kb, table 4) of the TWEEQ results based on 14 equilibria (3 independent reactions) for the garnet-chlorite-plagioclase-quartz-$H_2O$ assemblages in samples 1001 and 2025A (fig. 14A) and 29 equilibria (4 independent reactions) for the garnet-chlorite-plagioclase-

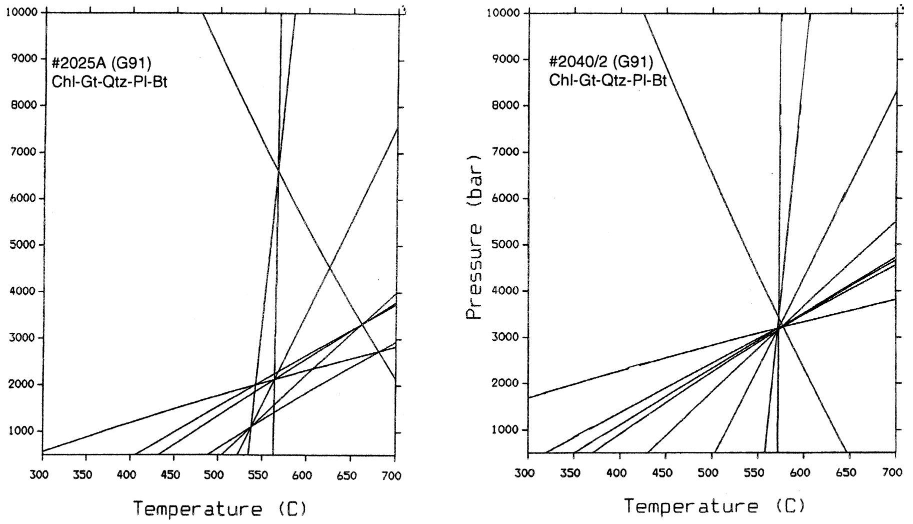

Fig. 13. TWEEQ computation of water-free equilibria among chlorite, garnet, biotite, plagioclase and quartz in the system $CaO\text{-}MgO\text{-}FeO\text{-}K_2O\text{-}Al_2O_3\text{-}SiO_2$ calculated for samples 2025A (A) and 2040/2 (B) from File Lake Gordon and others (1991).

quartz-biotite-$H_2O$ assemblage in sample 2040-2 (fig. 14B). Support for the chlorite solution data comes also from the fact that TWEEQ results all plot closely clustered (table 4) and are consistent with previous estimates (Gordon and others, 1991).

*Iberian Massif.*—Chlorites 6, 9, and 10 were excluded based on chemical criteria. Three assemblages corresponding to different conditions of metamorphism were identified by Arenas and others (1995) : M1 is characterized by the Chl-Gt-Qtz-Ep assemblage, M3 by Chl-Gt-Qtz-Pl, and M4 by Chl-Gt-Qtz-Pl-Bt. Equi-

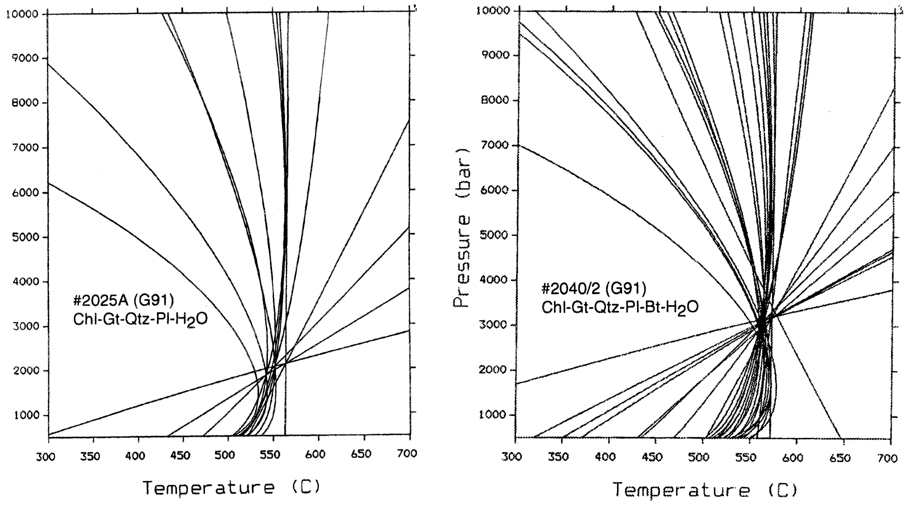

Fig. 14. TWEEQ computation of equilibria among chlorite, garnet, plagioclase, and quartz and $H_2O$ (A) for sample 2025A and chlorite, garnet, plagioclase, biotite, quartz, and $H_2O$ (B) for sample 2040/2 from File Lake (Gordon and others 1991).

librium conditions were estimated for these assemblages (table 4) using the rim composition of garnet.

P-T conditions inferred for mineral assemblages contemporaneous with M1 and M3 from the anhydrous Gt-Chl-Qtz-Ep or Pl assemblages are listed in column "I" (table 4). Except for the pair 3Chl-3Gtr, the temperatures defined by the Gt-Chl equilibrium are in excellent agreement with the previous estimates of Arenas and others (1995), although they are at least 80°C higher than those obtained with various empirical Gt-Chl thermometers, such as that calibrated by Grambling (1990) (column "II" in table 4). The pressure conditions estimated using a simple ideal activity model for epidote ($aCz = XAl^3$) and the standard state properties from Evans (1990) are also in agreement with the previous estimates, except for 3Chl-3Gtr, which are believed to be out of equilibrium. When considering water as an additional phase, the P-T conditions are constrained by 14 equilibria (3 independent reactions). The INTERSX $1\sigma$ standard deviation obtained when all equilibria are included is less than 12°C and less than 900 bar for all samples except 3Chl-3Gtr (column "III" in table 4). These results led credence to the equilibrium assumption between garnet, chlorite, epidote or plagioclase and quartz with a fluid of water activity close to unity. They also suggest that the chlorite data are compatible with the clinozoisite data calculated by Evans (1990), garnet data from Berman (1990), and plagioclase from Furhman and Lindsley (1988).

For samples contemporaneous with the M4 metamorphic episode, we report only the results of calculations performed with two biotite compositions (9Bt1 and 2), because the Chl-Bt Fe-Mg exchange reactions calculated with the other biotite compositions are located at unrealistic pressure (above 10 kb), as it was observed for the File Lake samples. For the two assemblages listed in table 4, the calculated P-T conditions are also in good agreement with the previous estimates. In particular, the calculated pressure conditions are clearly lower than in the case of M1 and M3, as was suggested by Arenas and others (1995). Also satisfactory is the relatively low scatter observed when considering chloritoid (XMg = 0.185, XFe = 0.835, Cld7) in addition to the chlorite-garnet-biotite-plagioclase-quartz-$H_2O$ assemblage (169 reactions, 6 independent equilibria).

## CONCLUSIONS AND PERSPECTIVES

The Mg-amesite and daphnite standard state properties calculated in the present study are compatible with the thermodynamic data of clinochlore from Berman (1988), Mg-sudoite and -carpholite data from Vidal and others (1992), Fe-chloritoid from Vidal and others (1995), and the Chl-Cld Fe-Mg exchange thermometer of Vidal and others (1999). Selected chlorite-garnet natural data suggest that the chlorite model is also consistent with the solid solution properties from Berman (1990) for garnet, Fuhrman and Lindsley (1988) for plagioclase, and Evans (1990) for epidote. However, large discrepancies are observed between the temperatures obtained from empirical Fe-Mg exchange thermometers and the temperatures calculated in the present study, so that additional work on garnet-chlorite assemblages is required to confirm the apparent consistency between the garnet solid solution model from Berman (1990) and the chlorite model proposed in the present study. The calculated $W_{AlMg}$ and $W_{AlFe}$ parameters are similar in magnitude and sign to the same parameters calculated by Mäder and others (1994) for the M2 site of hornblendes as well as by Aranovitch (1991) for orthopyroxene and by Berman and others (1995) for clinopyroxene. In comparison to other chlorite solution data reported in the literature, our data were calibrated from experimental and natural data covering a wide range of P-T conditions, so that they do not have to be extrapolated outside the calibration range to be used for P-T estimates of natural samples. They are reasonably consistent with the ~60 experimental phase equilibria and solubility experimental constraints obtained by various authors in the simplified MgO-(FeO)-$Al_2O_3$-$SiO_2$-$H_2O$ chemical system as well as most of the 185 natural data used in this study.

At present, the proposed chlorite model only pertains to chlorites with a Si-content $< 3$. This limit was imposed by the use of clinochlore as the most Si-rich endmember on the serpentine-amesite binary. As a consequence, the model can be used for trioctahedral chlorites that occur in most aluminous metapelites but not for the di/trioctahedral sudoite which often shows a Si-content $> 3$. An extension of the present model to more siliceous chlorite compositions should be a significant improvement since it would provide additional constraints such as the composition of sudoite and trioctahedral chlorites coexisting at low temperature, medium to low-pressure conditions (see above). In the absence of additional experimental results, these constraints are particularly important to determine more precisely the individual magnitudes of $W\square_{Al}$, $W\square_{Mg}$, and $W\square_{Fe}$ which are poorly constrained at present. However, the extension of the model to more siliceous chlorite compositions will require additional considerations, such as the reciprocal nature of chlorites (Holland and others, 1998) which has been overlooked in the present study.

The use of several chlorite endmembers makes the estimation of paleo-pressure and -temperature conditions possible for high-variance parageneses ($> 1$) which is not possible when using only one chlorite endmember (classically clinochlore). In particular, reliable pressure estimates can be made for the common Chl-Qtz-Car or Cld or Gt bearing rocks (app.) devoid of aluminosilicates, whereas such estimates are impossible when using only one chlorite endmember. Therefore, it is expected that a more continuous *spatial* assessment of the metamorphic P-T conditions in the field will be possible. Another potential use of the chlorite data calibrated in this study is the calculation of P-T paths using different chlorite generations coexisting in the same thin section. The location of these different generations are often controlled by the rock's microstructure. Therefore, different P-T estimates for various chlorite compositions associated with different structures could be used to constrain the ***P-T**-deformation evolution* from a minimal amount of sample (that is one thin section). Particularly interesting is the use of the chlorite composition to provide constraints on the late stage (in the greenschist facies) shape of the retrograde path followed by HP-LT rocks. Such constraints are generally difficult to obtain since the rock mineralogy does not change significantly at greenschist facies conditions, even though this information is required to build thermomechanical models at the regional scale. Application of examples and a comparison of P-T estimates based on chlorite compositions with estimates based on phengite compositions are discussed in Vidal and Parra (2000).

## ACKNOWLEDGMENTS

Thanks are due to P. Agard and R. Bousquet for helpful discussions and for sharing their detailed knowledge of the carpholite-samples used in this study and to R. Oberhänsli for providing chlorite and chloritoid analyses from the Lycian nappes. We are grateful for critical comments by F. Brunet, C. Chopin, and G. Simpson on early drafts of the manuscript and constructive reviews by C. de Capitani, D.M. Jenkins, and an anonymous reviewer.

## APPENDIX

*Natural data used for the thermodynamic extraction.*

The first column lists the molar fraction of atom per site for chlorites (CHL) (see table 1), chloritoid (CLD), and carpholite (CAR).

Column (I) lists the temperature location of equilibrium (4) (not calculated when $XSud < 0.045$, see text). For the Chl-Cld-Qtz assemblages, $T_{(4)}$ is read at pressure determined by the equilibrium Mg-Sud + Daph + Mg-Am = Fe-Cld + Clin +$H_2O$ when $T_{(4)} < T_{(15)}$ or Mg-Am + Qtz = Mg-Cld + Clin + $H_2O$ when $T_{(4)} > T_{(15)}$ (circles on fig. 9A and B).

Column (II) lists the P-T conditions of the sudoite-absent invariant point where Mg-Am, Clin, Daph, Fe, and Mg-Cld, Qtz, and $H_2O$ coexist (squares on fig. 9A, B and C).

Column (III) lists the temperature estimated with the LnKd ($= (Fe/Mg)^{Cld}/(Fe/Mg)^{Chl}$) = f(T) equation from Vidal and others (1999).

Column IV : Sud-Cld-Qtz-$H_2O$ equilibrium temperature at fixed pressure (4 kb).

(A) Goffé and Bousquet (1997), (B) Bousquet (1998), (C) Cannic and others (1996), (D) Bouybaouène and others (1995), (E) Bröcker and others (1993), (F) Massonne and Schreyer (1989), (G) based on the stability of rectorite + pyrophyllite as determined by Vidal (1997), (H) Oberhänsli and others (2000), (I) Theye and Seidel (1991), Theye and others (1992), (J and L) metapelitic assemblages, (K and M) metabasitic assemblages.

t.s.: this study; A99: Agard (1999); A94: Azanon (1994); AG98: Azanon and Goffé (1997); AE84: Asworth and Ervigen (1984); B98: Bousquet (1998); C85: Cathelineau and Nieva (1985); C79: Chopin (1979); CM84: Chopin and Monie (1984); C93: De caritat and others (1993); G98: Giorgetti and others (1998); G87: Ghent and others (1987); L98: Leoni, Sartori, and Tamponi (1998); OK94: Okay and Kelley (1994); P81: Paradis (1981); T92: Theye and others (1992); R94: Rahn and others (1994); W86: Walshe (1986); HV91: Hillier and Velde (1991); VB98: Vuichard and Ballèvre (1988); V99: Vidal and others (1999).

Appendix tables on following page

## APPENDIX

## *Natural data used for the thermodynamic extraction*

| | Chlorite-chloritoid-quartz | | | | | | | | | Sample | I | | II | | III | Original estimate | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | T °C | P Kb | T °C | P Kb | T °C | T °C | P Kb | |
| CHL | [Si | Al]$_{T2}$ | [Mg | Fe | Al | □]$_{M1}$ | [Mg | Fe | Al]$_{(M2+M3)}$ | | | | | | | | | |
| CLD | [Mg | Fe] | | | | | | | | | | | | | | | | |
| | Dauphinois zone (Western Alps) | | | | | | | | | | | | | | | | | |
| CHL | .324 | .671 | .210 | .227 | .351 | .211 | .427 | .463 | .106 | Mad-II | 355 | 6 | 301 | 6.9 | 315 | 300±50 | 5±2 | V99 |
| CLD | .077 | .908 | | | | | | | | | | | | | | | | |
| CHL | .263 | .737 | .189 | .230 | .483 | .098 | .428 | .519 | .049 | Mad-III | | P < 0 | 312 | 2.8 | 326 | | | |
| CLD | .074 | .920 | | | | | | | | | | | | | | | | |
| CHL | .280 | .717 | .172 | .140 | .462 | .226 | .480 | .393 | .113 | Mad-IV | | P < 0 | 255 | 3.7 | 273 | | | |
| CLD | .077 | .889 | | | | | | | | | | | | | | | | |
| CHL | .391 | .609 | .094 | .164 | .306 | .436 | .285 | .496 | .218 | Mad32 | 275 | 11 | 366 | 10.3 | 412 | | | ts |
| CLD | .077 | .908 | | | | | | | | | | | | | | | | |
| | Valaisan zone (Central Alps) | | | | | | | | | | | | | | | | | |
| CHL | .314 | .686 | .200 | .332 | .392 | .076 | .353 | .586 | .038 | CH1 | 501 | 11.1 | 483 | 11.1 | 522 | 500±30(A) | 14±1 (A) | B98 |
| CLD | .110 | .830 | | | | | | | | | | | | | | | 12±2 (B) | |
| CHL | .334 | .665 | .302 | .255 | .340 | .102 | .511 | .433 | .051 | Chl8 | 440 | 11.1 | 466 | 12.3 | 492 | 470-550 | ~13 (C) | V99 |
| CLD | .188 | .796 | | | | | | | | | | | | | | | | |
| CHL | .322 | .678 | .270 | .253 | .365 | .112 | .485 | .455 | .056 | Chl6 | 444 | 10.1 | 480 | 11.6 | 518 | | | V99 |
| CLD | .180 | .780 | | | | | | | | | | | | | | | | |
| CHL | .323 | .676 | .284 | .250 | .365 | .101 | .502 | .441 | .051 | Chl9 | 473 | 8.9 | 420 | 9.4 | 440 | | | V99 |
| CLD | .149 | .794 | | | | | | | | | | | | | | | | |
| CHL | .333 | .665 | .222 | .388 | .344 | .045 | .353 | .617 | .023 | Chl39 | 552 | 14.6 | 511 | 14.6 | 541 | | | V99 |
| CLD | .116 | .868 | | | | | | | | | | | | | | | | |
| CHL | .326 | .674 | .155 | .322 | .373 | .150 | .297 | .616 | .075 | chl57 | 382 | 7.9 | 420 | 9.5 | 448 | | | V99 |
| CLD | .072 | .873 | | | | | | | | | | | | | | | | |
| CHL | .313 | .687 | .265 | .237 | .388 | .110 | .495 | .443 | .055 | chl56 | 470 | 9.4 | 440 | 9.7 | 472 | | | V99 |
| CLD | .165 | .795 | | | | | | | | | | | | | | | | |
| CHL | .321 | .679 | .229 | .335 | .369 | .067 | .392 | .573 | .034 | Fen150 | 442 | 12.8 | 512 | 12.8 | 545 | | | ts |
| CLD | .134 | .854 | | | | | | | | | | | | | | | | |
| CHL | .336 | .664 | .253 | .339 | .345 | .062 | .413 | .554 | .031 | Fen149 | 437 | 13.4 | 494 | 13.5 | 515 | | | ts |
| CLD | .137 | .872 | | | | | | | | | | | | | | | | |
| | Beni Mzala window (Upper sebtides) | | | | | | | | | | | | | | | | | |
| CHL | .336 | .662 | .343 | .196 | .346 | .115 | .598 | .341 | .058 | chl65 | 440 | 10.7 | 418 | 10.2 | 438 | < 410 (D) | < 8 (D) | V99 |
| CLD | .220 | .768 | | | | | | | | | | | | | | | | |
| CHL | .333 | .667 | .246 | .254 | .340 | .159 | .451 | .466 | .080 | chl34 | 372 | 9.4 | 377 | 9.6 | 397 | | | V99 |
| CLD | .117 | .880 | | | | | | | | | | | | | | | | |
| CHL | .328 | .672 | .269 | .248 | .352 | .132 | .483 | .445 | .066 | chl28 | 425 | 8 | 370 | 6.8 | 380 | | | V99 |
| CLD | .120 | .868 | | | | | | | | | | | | | | | | |
| CHL | .331 | .668 | .237 | .262 | .336 | .164 | .435 | .481 | .082 | chl39 | 370 | 9 | 420 | 11 | 443 | | | V99 |
| CLD | .131 | .869 | | | | | | | | | | | | | | | | |
| CHL | .327 | .670 | .310 | .229 | .353 | .108 | .543 | .402 | .054 | chl64 | 448 | 10.8 | 437 | 10.5 | 459 | > 430 (D) | > 10 (D) | V99 |
| CLD | .192 | .799 | | | | | | | | | | | | | | | | |
| CHL | .344 | .656 | .418 | .132 | .311 | .138 | .706 | .223 | .069 | chl22X | 400 | 9 | 430 | 13.2 | 452 | | | V99 |
| CLD | .348 | .636 | | | | | | | | | | | | | | | | |
| CHL | .338 | .662 | .371 | .212 | .324 | .093 | .607 | .347 | .046 | chl22 | 457 | 12.2 | 462 | 12.7 | 477 | | | V99 |
| CLD | .248 | .748 | | | | | | | | | | | | | | | | |
| | Monte Rosa (Alps) | | | | | | | | | | | | | | | | | |
| CHL | .381 | .620 | .640 | .085 | .239 | .036 | .867 | .115 | .018 | MZ | - | - | 504 | 16.2 | 501 | 525±25 | 16 | CM84 |
| CLD | .613 | .397 | | | | | | | | | | | | | | | | |
| | Tinos Island, Greece (Egean domain) | | | | | | | | | | | | | | | | | |
| CHL | .299 | .701 | .187 | .342 | .437 | .034 | .342 | .627 | .017 | k1b/50 | - | - | 405 | 6.6 | 423 | 440-470 (E) | | ts |
| CLD | .076 | .918 | | | | | | | | | | | | | | | | |
| CHL | .319 | .681 | .203 | .350 | .385 | .062 | .352 | .605 | .031 | k1b/70 | 520 | 13.2 | 505 | 12.4 | 542 | | | ts |
| CLD | .116 | .866 | | | | | | | | | | | | | | | | |
| CHL | .310 | .690 | .191 | .326 | .414 | .069 | .351 | .601 | .035 | k1b/67 | 545 | 7.7 | 420 | 7.7 | 443 | | | ts |
| CLD | .083 | .845 | | | | | | | | | | | | | | | | |
| CHL | .337 | .663 | .261 | .241 | .405 | .092 | .494 | .457 | .046 | IST/172 | 480 | 10.3 | 454 | 10.3 | 491 | | | ts |
| CLD | .169 | .785 | | | | | | | | | | | | | | | | |
| CHL | .322 | .678 | .268 | .258 | .386 | .088 | .485 | .468 | .044 | IST/173 | 502 | 10.7 | 460 | 10.5 | 492 | | | ts |
| CLD | .167 | .806 | | | | | | | | | | | | | | | | |
| | Gran Paradiso (Alps) | | | | | | | | | | | | | | | | | |
| CHL | .380 | .620 | .475 | .186 | .257 | .082 | .689 | .270 | .041 | 6-298c | 422 | 14 | 423 | 14 | 440 | 500±50 (F) | 15 (F) | C79,81 |
| CLD | .276 | .721 | | | | | | | | | | | | | | | | |
| CHL | .418 | .582 | .551 | .249 | .174 | .026 | .680 | .307 | .013 | 7-172c1 | ***557*** | 23 | 542 | 21.7 | 523 | | | C79,81 |
| CLD | .332 | .678 | | | | | | | | | | | | | | | | |
| CHL | .418 | .582 | .551 | .249 | .174 | .026 | .680 | .307 | .013 | 7-172c2 | ***557*** | 23 | 488 | 19.5 | 467 | | | C79,81 |
| CLD | .291 | .719 | | | | | | | | | | | | | | | | |
| CHL | .418 | .582 | .613 | .152 | .170 | .065 | .776 | .192 | .033 | GP 9 | 382 | 15.6 | 415 | 17.2 | 398 | | | C79,81 |
| CLD | .349 | .621 | | | | | | | | | | | | | | | | |
| CHL | .436 | .564 | .648 | .144 | .130 | .078 | .786 | .175 | .039 | GP 12 | 312 | 14.2 | 476 | 22.1 | 454 | | | C79,81 |
| CLD | .436 | .556 | | | | | | | | | | | | | | | | |
| CHL | .313 | .688 | .254 | .318 | .381 | .047 | .434 | .542 | .023 | 6-80 Chl1 | - | - | 462 | 10.2 | 487 | | | C79,81 |
| CLD | .133 | .849 | | | | | | | | | | | | | | | | |
| CHL | .291 | .710 | .230 | .271 | .431 | .068 | .443 | .523 | .034 | 6-80 Chl2 | ***>600*** | | 426 | 7.5 | 456 | | | C79,81 |
| CLD | .127 | .856 | | | | | | | | | | | | | | | | |
| CHL | .314 | .686 | .270 | .293 | .396 | .042 | .467 | .508 | .021 | 6-80 Chl3 | - | - | 416 | 8.3 | 434 | | | C79,81 |
| CLD | .127 | .856 | | | | | | | | | | | | | | | | |
| CHL | .380 | .618 | .490 | .199 | .236 | .076 | .684 | .278 | .038 | 7-172/2 | 432 | 13.5 | 485 | 16 | 487 | | | ts |
| CLD | .316 | .655 | | | | | | | | | | | | | | | | |
| CHL | .376 | .623 | .487 | .198 | .251 | .064 | .688 | .280 | .032 | 7-172/3 | 478 | 14.9 | 485 | 15.2 | 488 | | | ts |
| CLD | .316 | .655 | | | | | | | | | | | | | | | | |
| CHL | .394 | .606 | .513 | .200 | .221 | .066 | .694 | .271 | .033 | 7-172/4 | 440 | 14.6 | 480 | 16.5 | 476 | | | ts |
| CLD | .316 | .655 | | | | | | | | | | | | | | | | |
| CHL | .409 | .588 | .540 | .207 | .181 | .071 | .696 | .267 | .036 | 7-172/6 | 380 | 14 | 467 | 17.6 | | | | ts |
| CLD | .290 | .641 | | | | | | | | | | | | | | | | |
| CHL | .408 | .591 | .536 | .218 | .193 | .054 | .692 | .281 | .027 | 7-172/11 | 446 | 15.5 | 482 | 17.3 | 468 | | | |
| CLD | .290 | .641 | | | | | | | | | | | | | | | | |

## APPENDIX

*(continued)*

| **Chlorite-chloritoid-quartz** | | | | | | | | | | Sample | I | | II | | III | Original estimate | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | T | P | T | P | T | T | P | |
| **CHL** | **[Si** | **Al]$_{T2}$** | **[Mg** | **Fe** | **Al** | **□]$_{M1}$** | **[Mg** | **Fe** | **Al]$_{(M2+M3)}$** | | °C | Kb | °C | Kb | °C | °C | Kb | |
| **CLD** | **[Mg** | **Fe]** | | | | | | | | | | | | | | | | |
| New caledonia | | | | | | | | | | | | | | | | | | |
| CHL | .292 | .709 | .220 | .376 | .419 | .000 | .369 | .632 | .000 | 23913.000 | - | - | 415 | 7.5 | 432 | 410 ± 20 | 11 | G87 |
| CLD | .088 | .943 | | | | | | | | | | | | | | | | |
| CHL | .327 | .673 | .476 | .175 | .350 | .001 | .730 | .269 | .000 | 37101.000 | - | - | 480 | 11.6 | 496 | 560 ± 40 | 12 ± 1 | G87 |
| CLD | .370 | .676 | | | | | | | | | | | | | | | | |
| Massif Armoricain, France (Hercynian belt) | | | | | | | | | | | | | | | | | | |
| CHL | .294 | .706 | .124 | .288 | .419 | .169 | .274 | .638 | .084 | D44_15 | 405 | 6.2 | 437 | 7.5 | 477 | 330-420 (G) | 2 | P81 |
| CLD | .069 | .844 | | | | | | | | | | | | | | | | |
| CHL | .265 | .736 | .172 | .241 | .483 | .104 | .395 | .553 | .052 | D44_17 | 540 | 4 | 379 | 4 | 407 | | | P81 |
| CLD | .088 | .855 | | | | | | | | | | | | | | | | |
| Lycian nappes, Turkey (Egean domain) | | | | | | | | | | | | | | | | | | |
| CHL | .423 | .578 | .370 | .131 | .160 | .339 | .612 | .217 | .170 | O.6.3. | 220 | 16 | 320 | 15 | 297 | 350±30 | 3±1 | AE84 |
| CLD | .187 | .801 | | | | | | | | | | | | | | 350±50 (H) | 10 (H) | |
| CHL | .320 | .680 | .271 | .215 | .371 | .143 | .516 | .411 | .071 | O.23.6. | 385 | 8 | 425 | 7 | 396 | | - | AE84 |
| CLD | .146 | .846 | | | | | | | | | | | | | | | | |
| CHL | .322 | .678 | .278 | .186 | .356 | .179 | .544 | .364 | .089 | Chl10 | 385 | 9.7 | 402 | 10.3 | 432 | | | ts |
| CLD | .189 | .794 | | | | | | | | Cld23 | | | | | | | | |
| CHL | .325 | .674 | .301 | .188 | .348 | .162 | .565 | .353 | .081 | Chl14 | 391 | 10.2 | 391 | 10.2 | 414 | | | ts |
| CLD | .189 | .794 | | | | | | | | Cld23 | | | | | | | | |
| CHL | .361 | .637 | .318 | .200 | .284 | .198 | .552 | .347 | .099 | Chl24 | 325 | 10 | 390 | 12.6 | 416 | | | ts |
| CLD | .185 | .799 | | | | | | | | Cld27 | | | | | | | | |
| CHL | .342 | .655 | .314 | .208 | .311 | .167 | .550 | .365 | .084 | Chl25 | 360 | 10 | 409 | 12 | 430 | | | ts |
| CLD | .189 | .794 | | | | | | | | Cld23 | | | | | | | | |
| CHL | .338 | .662 | .300 | .208 | .324 | .168 | .541 | .375 | .084 | Chl26 | 369 | 9.7 | 410 | 11.4 | 417 | | | ts |
| CLD | .185 | .799 | | | | | | | | Cld27 | | | | | | | | |
| Emilius Klippe (Alps) | | | | | | | | | | | | | | | | | | |
| CHL | .387 | .614 | .509 | .228 | .251 | .012 | .686 | .308 | .006 | ASC16 | - | - | 537 | 16 | 535 | 550±50 | 15-20 | VB88 |
| CLD | .322 | .634 | | | | | | | | | | | | | | | | |
| CHL | .387 | .614 | .509 | .228 | .251 | .012 | .686 | .308 | .006 | ASC16 | - | - | 526 | 16.1 | 523 | | | VB88 |
| CLD | .326 | .665 | | | | | | | | | | | | | | | | |
| CHL | .415 | .585 | .478 | .260 | .187 | .075 | .624 | .339 | .038 | AGN6/1 | >600 | | 584 | 25 | 587 | | | VB88 |
| CLD | .323 | .662 | | | | | | | | | | | | | | | | |
| CHL | .375 | .625 | .522 | .212 | .269 | .003 | .712 | .289 | .002 | AGN6 | - | - | 534 | 15 | 535 | | | VB88 |
| Andalusia (Betic chain) | | | | | | | | | | | | | | | | | | |
| CHL | .310 | .691 | .357 | .192 | .384 | .067 | .628 | .338 | .034 | TV903 | >600 | | 476 | 11 | 503 | 400-500 | 8-15 | A94, AG97 |
| CLD | .271 | .704 | | | | | | | | | | | | | | | | |
| CHL | .323 | .677 | .184 | .345 | .383 | .088 | .333 | .623 | .044 | 921c | 480 | 12 | 450 | 12 | 456 | | | A94, AG97 |
| CLD | .085 | .905 | | | | | | | | | | | | | | | | |
| CHL | .336 | .664 | .360 | .206 | .346 | .088 | .608 | .348 | .044 | TV21 | 495 | 11.5 | 460 | 11.5 | 481 | | | A94, AG97 |
| CLD | .247 | .734 | | | | | | | | | | | | | | | | |
| CHL | .332 | .668 | .275 | .179 | .354 | .192 | .548 | .356 | .096 | I19 | 370 | 10 | 365 | 10 | 388 | | | A94, AG97 |
| CLD | .168 | .823 | | | | | | | | | | | | | | | | |
| CHL | .357 | .643 | .442 | .144 | .291 | .123 | .708 | .231 | .062 | Sal56 | 397 | 13 | 397 | 13 | 413 | | | A94, AG97 |
| CLD | .301 | .663 | | | | | | | | | | | | | | | | |
| CHL | .376 | .625 | .490 | .122 | .265 | .123 | .752 | .187 | .062 | Sal61 | 375 | 13 | 410 | 15 | 417 | | | A94, AG97 |
| CLD | .372 | .614 | | | | | | | | | | | | | | | | |
| CHL | .347 | .654 | .413 | .192 | .335 | .061 | .662 | .308 | .030 | CONJ-8 | >600 | | 415 | 11 | 425 | | | A94, AG97 |
| CLD | .249 | .743 | | | | | | | | | | | | | | | | |
| CHL | .310 | .691 | .357 | .192 | .384 | .067 | .628 | .338 | .034 | TV903 | 600 | 15 | 472 | 11 | 503 | | | A94, AG97 |
| CLD | .271 | .704 | | | | | | | | | | | | | | | | |
| CHL | .334 | .666 | .290 | .245 | .364 | .101 | .514 | .435 | .050 | CT2 | 455 | 11 | 462 | 12 | 492 | | | A94, AG97 |
| CLD | .188 | .796 | | | | | | | | | | | | | | | | |
| Kreta, Hellenides((Egean domain) | | | | | | | | | | | | | | | | | | |
| CHL | .320 | .680 | .188 | .342 | .365 | .105 | .336 | .612 | .053 | k76/54 | 430 | 9 | 415 | 9 | 434 | 350 ± 50 | 8 ± 2 | T92 |
| CLD | .080 | .905 | | | | | | | | | | | | | | | | |
| CHL | .385 | .615 | .465 | .145 | .230 | .160 | .701 | .219 | .080 | K86/90 | 310 | 12 | 420 | 16 | 428 | | | T92 |
| CLD | .330 | .655 | | | | | | | | | | | | | | | | |
| Peloponnese, Hellenides (Egean domain) | | | | | | | | | | | | | | | | | | |
| CHL | .359 | .640 | .390 | .145 | .283 | .183 | .663 | .246 | .091 | Pel34 | 330 | 11 | 337 | 11 | 345 | 450 ± 50(I) | 15 ± 2(I) | ts |
| CLD | .322 | .658 | | | | | | | | | | | | | | | | |
| CHL | .347 | .651 | .460 | .120 | .304 | .115 | .737 | .193 | .058 | Pel45 | 410 | 15 | 375 | 10 | 380 | | | ts |
| CLD | .221 | .759 | | | | | | | | 43 | | | | | | | | |
| CHL | .359 | .640 | .390 | .145 | .283 | .183 | .663 | .246 | .091 | Pel34 | 333 | 11.7 | 333 | 11.7 | 345 | | | ts |
| CLD | .221 | .759 | | | | | | | | 43 | | | | | | | | |
| CHL | .358 | .639 | .312 | .311 | .296 | .080 | .479 | .477 | .040 | Tg963B24 | 430 | 12.5 | 470 | 14.3 | 486 | | | ts |
| CLD | .163 | .837 | | | | | | | | B2508 | | | | | | | | |
| CHL | .326 | .674 | .278 | .278 | .351 | .094 | .475 | .475 | .047 | Tg963B20 | 445 | 11.3 | 455 | 12.2 | 504 | | | ts |
| CLD | .172 | .828 | | | | | | | | B16 | | | | | | | | |
| CHL | .302 | .698 | .220 | .263 | .411 | .105 | .429 | .513 | .053 | Tg963B140 | 475 | 10.2 | 505 | 11.5 | 563 | | | ts |
| CLD | .172 | .828 | | | | | | | | B18 | | | | | | | | |
| CHL | .346 | .651 | .297 | .288 | .307 | .109 | .478 | .463 | .054 | Tg963B5 | 398 | 11.1 | 408 | 11.6 | 420 | | | ts |
| CLD | .136 | .864 | | | | | | | | B7 | | | | | | | | |
| CHL | .336 | .662 | .269 | .299 | .342 | .090 | .451 | .501 | .045 | Tg963B47 | 445 | 11.5 | 480 | 13 | 507 | | | ts |
| CLD | .159 | .841 | | | | | | | | B49 | | | | | | | | |
| CHL | .326 | .674 | .267 | .277 | .355 | .101 | .464 | .481 | .051 | Tg963B40 | 441 | 11 | 441 | 11 | 465 | | | ts |
| CLD | .149 | .851 | | | | | | | | B38 | | | | | | | | |
| CHL | .361 | .636 | .340 | .274 | .283 | .103 | .522 | .420 | .051 | Tg964M119 | 395 | 11.9 | 380 | 11.2 | 378 | | | ts |
| CLD | .139 | .861 | | | | | | | | M121 | | | | | | | | |
| CHL | .345 | .653 | .331 | .271 | .307 | .091 | .521 | .426 | .046 | Tg964M127 | 442 | 11.5 | 402 | 9.7 | 407 | | | ts |
| CLD | .150 | .850 | | | | | | | | M128 | | | | | | | | |
| CHL | .346 | .654 | .330 | .273 | .318 | .079 | .523 | .433 | .040 | Tg964N142 | 485 | 10.2 | 410 | 8.1 | 414 | | | ts |
| CLD | .152 | .848 | | | | | | | | N140 | | | | | | | | |
| CHL | .362 | .636 | .341 | .279 | .290 | .089 | .524 | .429 | .044 | Tg964N137 | 426 | 11.4 | 396 | 10.4 | 398 | | | ts |
| CLD | .145 | .855 | | | | | | | | N136 | | | | | | | | |
| CHL | .267 | .730 | .255 | .291 | .475 | .001 | .469 | .537 | .001 | 7ch1/III | - | - | 515 | 9.2 | 572 | 505-540 | 6.5-9 | A95 |
| CLD | .185 | .830 | | | | | | | | 7cl1 | | | | | | | | |
| CHL | .320 | .677 | .291 | .322 | .357 | .031 | .467 | .516 | .015 | 8ch1/III | - | - | 458 | 10.4 | 474 | | | A95 |
| CLD | .140 | .825 | | | | | | | | 8cl1 | | | | | | | | |

## Appendix

*(continued)*

| Chlorite-carpholite-quartz | | | | | | | | | | Sample | I | | Original estimate | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CHL | [Si | Al]$_{T2}$ | [Mg | Fe | Al | □]$_{M1}$ | [Mg | Fe | Al]$_{(M2+M3)}$ | | T °C | P kb | T °C | P kb | |
| CAR | [Mg | Fe] | | | | | | | | | | | | | |
| CHL | .366 | .630 | .252 | .390 | .269 | .089 | .374 | .579 | .045 | Rf941/F15 | 337 | 15 | 300-350 | 10-15 | A99 |
| CAR | .440 | .560 | | | | | | | | | | | | | |
| CHL | .365 | .635 | .264 | .322 | .287 | .127 | .420 | .512 | .064 | Rf942/F54 | 332 | 12.5 | | | A99 |
| CAR | .440 | .560 | | | | | | | | | | | | | |
| CHL | .366 | .630 | .252 | .390 | .269 | .089 | .374 | .579 | .045 | Rf943/F38 | 338 | 15 | | | A99 |
| CAR | .440 | .560 | | | | | | | | | | | | | |
| CHL | .333 | .666 | .192 | .400 | .334 | .074 | .307 | .639 | .037 | Pit944/J14 | 395 | 16.4 | | | A99 |
| CAR | .320 | .580 | | | | | | | | | | | | | |
| CHL | .361 | .639 | .232 | .252 | .297 | .219 | .422 | .459 | .109 | Gb944/O31 | 304 | 10.3 | | | A99 |
| CAR | .450 | .550 | | | | | | | | | | | | | |
| CHL | .344 | .655 | .205 | .355 | .316 | .125 | .342 | .594 | .062 | J874/H50 | 337 | 13.7 | | | A99 |
| CAR | .420 | .580 | | | | | | | | | | | | | |
| CHL | .365 | .632 | .236 | .412 | .271 | .081 | .345 | .602 | .040 | Ccs951/J35 | 347 | 15.5 | | | A99 |
| CAR | .380 | .620 | | | | | | | | | | | | | |
| CHL | .374 | .621 | .206 | .459 | .263 | .073 | .297 | .663 | .036 | Vaz951/L31 | 340 | 16 | | | A99 |
| CAR | .322 | .688 | | | | | | | | | | | | | |
| CHL | .353 | .645 | .252 | .313 | .313 | .123 | .417 | .519 | .061 | Vaz951/L33 | 351 | 12.9 | | | A99 |
| CAR | .435 | .565 | | | | | | | | | | | | | |
| CHL | .369 | .629 | .249 | .406 | .283 | .063 | .366 | .596 | .031 | Des952/M26 | 391 | 16.5 | | | A99 |
| CAR | .332 | .678 | | | | | | | | | | | | | |
| CHL | .339 | .661 | .292 | .277 | .326 | .105 | .486 | .462 | .053 | Bo955/N57 | 385 | 14.2 | | | A99 |
| CAR | .542 | .458 | | | | | | | | | | | | | |
| CHL | .348 | .650 | .295 | .323 | .305 | .077 | .457 | .500 | .039 | Bo951/J24 | 394 | 16.2 | | | A99 |
| CAR | .530 | .470 | | | | | | | | | | | | | |
| CHL | .352 | .648 | .305 | .306 | .300 | .089 | .476 | .477 | .045 | Mor954/J18 | 382 | 14.9 | 350-400 | 12-17 | A99 |
| CAR | .520 | .480 | | | | | | | | | | | | | |
| CHL | .353 | .647 | .239 | .402 | .305 | .053 | .354 | .595 | .027 | Mor951/J66 | 415 | 18.5 | | | A99 |
| CAR | .371 | .629 | | | | | | | | | | | | | |
| CHL | .394 | .605 | .532 | .181 | .213 | .074 | .718 | .244 | .037 | Pel943/K4 | 403 | 14.9 | | | A99 |
| CAR | .722 | .288 | | | | | | | | | | | | | |
| CHL | .354 | .645 | .221 | .395 | .296 | .088 | .337 | .602 | .044 | Pit943/M1 | 362 | 14.5 | | | A99 |
| CAR | .322 | .688 | | | | | | | | | | | | | |
| CHL | .365 | .633 | .310 | .347 | .279 | .064 | .450 | .505 | .032 | Ge951/M48 | 403 | 16.6 | | | A99 |
| CAR | .442 | .55 | | | | | | | | | | | | | |
| CHL | .375 | .622 | .285 | .361 | .280 | .074 | .421 | .532 | .037 | Ge951/M51 | 365 | 16.3 | | | A99 |
| CAR | .500 | .500 | | | | | | | | | | | | | |
| Mundin unit, Engadine window (Central Alps) | | | | | | | | | | | | | | | |
| CHL | .402 | .595 | .181 | .127 | .609 | .083 | .534 | .373 | .083 | Alp938a/7 | 432 | 11.8 | 350-400 | 11-13 (J)<br>10-12 (K) | B99 |
| CAR | .500 | .500 | | | | | | | | | | | | | |
| CHL | .404 | .596 | .385 | .191 | .205 | .218 | .595 | .295 | .109 | Alp944/7 | 262 | 10.1 | | | B99 |
| CAR | .720 | .280 | | | | | | | | | | | | | |
| CHL | .398 | .602 | .406 | .227 | .216 | .150 | .589 | .330 | .075 | Samp935/4 | 298 | 11.2 | | | B99 |
| CAR | .640 | .360 | | | | | | | | | | | | | |
| CHL | .355 | .644 | .350 | .218 | .342 | .090 | .547 | .340 | .045 | Saro942a/12 | 420 | 15.3 | | | B99 |
| CAR | .620 | .380 | | | | | | | | | | | | | |
| CHL | .395 | .603 | .385 | .208 | .222 | .185 | .588 | .317 | .093 | Nau947/2 | 285 | 10.5 | | | B99 |
| CAR | .647 | .320 | | | | | | | | | | | | | |
| CHL | .356 | .644 | .372 | .206 | .306 | .115 | .604 | .335 | .058 | Nau947/3 | 382 | 13.5 | | | B99 |
| CAR | .690 | .268 | | | | | | | | | | | | | |
| CHL | .422 | .577 | .383 | .187 | .212 | .218 | .597 | .292 | .109 | Nau947/4 | 263 | 9.6 | | | B99 |
| CAR | .645 | .311 | | | | | | | | | | | | | |
| CHL | .376 | .622 | .439 | .208 | .263 | .090 | .647 | .307 | .045 | Nau947/5 | 394 | 14.2 | | | B99 |
| CAR | .670 | .290 | | | | | | | | | | | | | |
| CHL | .389 | .611 | .386 | .198 | .246 | .170 | .602 | .308 | .085 | Nau947/6 | 308 | 10.8 | | | B99 |
| CAR | .649 | .312 | | | | | | | | | | | | | |
| CHL | .357 | .643 | .365 | .212 | .292 | .131 | .590 | .343 | .066 | Nau947/7 | 363 | 12.4 | | | B99 |
| CAR | .623 | .337 | | | | | | | | | | | | | |
| CHL | .379 | .621 | .398 | .217 | .252 | .133 | .601 | .329 | .066 | Eng9315b/13 | 339 | 11.8 | | | B99 |
| CAR | .607 | .291 | | | | | | | | | | | | | |
| CHL | .367 | .631 | .389 | .243 | .276 | .091 | .585 | .366 | .046 | Eng9315b/15 | 382 | 14.7 | | | B99 |
| CAR | .670 | .120 | | | | | | | | | | | | | |
| CHL | .413 | .587 | .370 | .211 | .228 | .191 | .574 | .327 | .096 | Eng9315b/16 | 280 | 10.1 | | | B99 |
| CAR | .610 | .390 | | | | | | | | | | | | | |
| CHL | .371 | .627 | .418 | .202 | .265 | .115 | .632 | .306 | .057 | Eng9315b/18 | 368 | 12.8 | | | B99 |
| CAR | .650 | .350 | | | | | | | | | | | | | |
| CHL | .355 | .644 | .345 | .264 | .300 | .090 | .537 | .411 | .045 | Cha931/2 | 392 | 15.1 | | | B99 |
| CAR | .621 | .379 | | | | | | | | | | | | | |
| CHL | .411 | .589 | .408 | .222 | .212 | .159 | .594 | .323 | .079 | Eng942/3 | 289 | 10.7 | | | B99 |
| CAR | .621 | .000 | | | | | | | | | | | | | |
| CHL | .406 | .593 | .430 | .181 | .196 | .193 | .635 | .268 | .097 | Eng942/4 | 272 | 9.9 | | | B99 |
| CAR | .690 | .268 | | | | | | | | | | | | | |
| CHL | .362 | .638 | .391 | .244 | .285 | .081 | .588 | .367 | .040 | Tun941/1 | 421 | 17.7 | | | B99 |
| CAR | .527 | .403 | | | | | | | | | | | | | |
| CHL | .357 | .643 | .365 | .260 | .299 | .075 | .558 | .398 | .038 | Eng942/2 | 326 | 11.5 | | | B99 |
| CAR | .499 | .466 | | | | | | | | | | | | | |
| CHL | .373 | .627 | .388 | .248 | .275 | .089 | .581 | .371 | .044 | Eng942/3 | 391 | 14.3 | | | B99 |
| CAR | .580 | .380 | | | | | | | | | | | | | |
| CHL | .369 | .630 | .385 | .267 | .269 | .078 | .564 | .391 | .039 | Eng942/13 | 407 | 14.6 | | | B99 |
| CAR | .499 | .466 | | | | | | | | | | | | | |

## Appendix

*(continued)*

| **Chlorite-carpholite-quartz**<br>**CHL $[Si\ Al]_{T2}[Mg\ Fe\ Al\ \square]_{M1}[Mg\ Fe\ Al]_{(M2+M3)}$**<br>**CAR $[Mg\ Fe]$** | Sample | I<br>T<br>°C | <br>P<br>kb | Original estimate<br>T<br>°C | <br>P<br>kb | Reference |
|---|---|---|---|---|---|---|
| Grison (upper unit), Engadine window (Central Alps) | | | | | | |
| CHL .354 .646 .271 .332 .312 .085 .428 .524 .043 | Prasug941/4 | 376 | 15.8 | 350-400 (1 ) | 12-16 (L) | B99 |
| CAR .526 .484 | | | | | 11-13 (M) | |
| CHL .365 .632 .275 .338 .270 .117 .420 .517 .059 | Prasug941/5 | 324 | 13.5 | | | B99 |
| CAR .502 .498 | | | | | | |
| CHL .351 .648 .264 .321 .306 .109 .425 .516 .054 | Prasug941c/3 | 353 | 14.4 | | | B99 |
| CAR .530 .470 | | | | | | |
| CHL .351 .648 .264 .321 .306 .109 .425 .516 .054 | Prasug941c/33 | 355 | 14.2 | | | B99 |
| CAR .505 .467 | | | | | | |
| | Saf942b/1 | 379 | 14.6 | | | B99 |
| CHL .346 .653 .281 .313 .311 .095 .447 .498 .048 | Chur941d/4 | 379 | 14.5 | | | B99 |
| CAR .483 .477 | | | | | | |
| CHL .332 .667 .254 .310 .339 .098 .426 .520 .049 | Chur941d/5 | 390 | 14.8 | | | B99 |
| CAR .480 .520 | | | | | | |
| CHL .358 .641 .237 .288 .344 .131 .421 .512 .066 | Chur941b/3 | 351 | 13.2 | | | B99 |
| CAR .510 .490 | | | | | | |
| CHL .345 .654 .253 .312 .311 .124 .417 .515 .062 | Tomil940/6 | 347 | 13.4 | | | B99 |
| CAR .491 .509 | | | | | | |
| CHL .327 .673 .273 .238 .358 .130 .500 .435 .065 | Vers941a/2 | 397 | 12.3 | | | B99 |
| CAR .460 .540 | | | | | | |
| CHL .369 .630 .385 .267 .269 .078 .564 .391 .039 | Vers941a/13 | 398 | 15.3 | | | B99 |
| CAR .580 .420 | | | | | | |

| **Chlorite-quartz (low-T samples)**<br>**CHL $[Si\ Al]_{T2}[Mg\ Fe\ Al\ \square]_{M1}[Mg\ Fe\ Al]_{(M2+M3)}$** | | I<br>T<br>°C | C88<br>T<br>°C | HV91<br>T<br>°C | Original estimate<br>T<br>°C | |
|---|---|---|---|---|---|---|
| CHL .453 .548 .156 .440 .095 .309 .220 .623 .154 | 1 | 175 | 291 | 190 | 190 | W86 |
| CHL .457 .542 .404 .382 .084 .130 .477 .451 .065 | 8 | 260 | 287 | 264 | 264 | W86 |
| CHL .468 .532 .351 .332 .064 .253 .448 .424 .126 | 6 | 180 | 281 | 264 | 264 | W86 |
| CHL .440 .561 .326 .452 .121 .101 .393 .545 .050 | 7 | 300 | 299 | 280 | 280 | W86 |
| CHL .448 .553 .359 .401 .105 .135 .436 .487 .067 | 11 | 258 | 294 | 315 | 315 | W86 |
| CHL .321 .679 .208 .295 .358 .139 .384 .546 .070 | CV | 410 | 375 | 375 | 375 | L98 |
| CHL .325 .674 .221 .266 .349 .163 .417 .501 .082 | MF | 378 | 375 | 375 | 375 | L98 |
| CHL .324 .675 .209 .272 .351 .167 .398 .518 .084 | MG | 370 | 373 | 325 | 325 | L98 |
| CHL .339 .661 .208 .253 .322 .217 .402 .490 .109 | CT | 338 | 364 | 300 | 300 | L98 |
| CHL .376 .623 .200 .250 .246 .304 .377 .471 .152 | BVG | 260 | 340 | 275 | 275 | L98 |
| CHL .314 .686 .217 .295 .372 .116 .399 .543 .058 | cv12 | 450 | 380 | 375 | 375 | L98 |
| CHL .338 .662 .205 .296 .324 .176 .373 .539 .088 | cv89 | 360 | 364 | 375 | 375 | L98 |
| CHL .328 .672 .215 .283 .345 .158 .397 .524 .079 | cv83 | 378 | 371 | 375 | 375 | L98 |
| CHL .327 .673 .198 .259 .347 .196 .390 .512 .098 | mf1 | 358 | 372 | 325 | 325 | L98 |
| CHL .351 .649 .321 .236 .299 .145 .534 .393 .072 | mf19 | 382 | 356 | 325 | 325 | L98 |
| CHL .344 .657 .250 .262 .313 .174 .446 .466 .087 | mf63 | 363 | 361 | 325 | 325 | L98 |
| CHL .322 .677 .217 .273 .354 .155 .408 .514 .078 | mg67 | 390 | 374 | 300 | 300 | L98 |
| CHL .327 .673 .200 .287 .345 .168 .376 .540 .084 | mg45 | 370 | 371 | 300 | 300 | L98 |
| CHL .332 .668 .215 .255 .335 .194 .413 .490 .097 | mg33 | 361 | 368 | 300 | 300 | L98 |
| CHL .339 .661 .227 .255 .322 .197 .424 .477 .098 | ct7 | 350 | 364 | 300 | 300 | L98 |
| CHL .339 .662 .189 .250 .324 .238 .379 .502 .119 | ct19 | 330 | 364 | 300 | 300 | L98 |
| CHL .372 .628 .177 .233 .257 .332 .360 .474 .166 | bvg12 | 270 | 343 | 275 | 275 | L98 |
| CHL .381 .619 .223 .264 .238 .275 .394 .468 .138 | bvg32 | 270 | 337 | 275 | 275 | L98 |
| CHL .345 .655 .247 .178 .309 .265 .499 .360 .133 | M34 | 312 | 360 | 350 | 350 | G98 |
| CHL .318 .682 .198 .238 .364 .200 .408 .491 .100 | M655 | 374 | 377 | 360 | 360 | G98 |
| CHL .331 .668 .237 .262 .336 .164 .435 .481 .082 | chl39 | 380 | 368 | 360 | 360 | G98 |
| CHL .365 .635 .077 .393 .270 .260 .143 .727 .130 | ON-5 | 257 | 347 | 155 | 155 | C93 |
| CHL .427 .573 .339 .405 .169 .087 .430 .512 .044 | Mf776 | 358 | 307 | 290 | 290 | R94 |
| CHL .483 .517 .366 .448 .068 .118 .418 .511 .059 | MF778 | 240 | 271 | 290 | 290 | R94 |
| CHL .461 .539 .391 .390 .107 .112 .467 .467 .056 | MRT96 | 282 | 285 | 290 | 290 | R94 |
| CHL .396 .604 .323 .333 .232 .113 .461 .475 .056 | MRT17 | 368 | 327 | 290 | 290 | R94 |
| CHL .434 .561 .353 .373 .156 .117 .452 .478 .059 | MRT24 | 305 | 300 | 290 | 290 | R94 |
| CHL .490 .510 .498 .279 .041 .182 .579 .324 .091 | ca1 | 175 | 266 | 180 | 180 | CN85 |
| CHL .499 .501 .461 .248 .041 .249 .566 .305 .125 | ca2 | 150 | 261 | 180 | 180 | CN85 |
| CHL .463 .537 .579 .234 .100 .086 .674 .272 .043 | ca5 | 350 | 284 | 240 | 240 | CN85 |
| CHL .473 .527 .616 .263 .070 .052 .680 .290 .026 | ca9 | 400 | 277 | 290 | 290 | CN85 |
| CHL .496 .504 .606 .294 .031 .069 .645 .313 .035 | ca10 | 275 | 263 | 290 | 290 | CN85 |
| CHL .469 .531 .541 .325 .086 .049 .605 .363 .024 | ca13 | 410 | 280 | 300 | 300 | CN85 |
| CHL .485 .512 .538 .323 .048 .091 .594 .356 .045 | ca14 | 260 | 268 | 300 | 300 | CN85 |
| CHL .320 .684 .169 .299 .381 .151 .334 .589 .075 | 44 | 353 | 378 | 350 | 350 | CN85 |
| CHL .495 .508 .241 .390 .063 .305 .324 .523 .153 | 7036-64 | 150 | 265 | 100 | 100 | HV91 |
| CHL .338 .644 .203 .346 .292 .160 .340 .580 .080 | 7036-58 | 340 | 353 | 250 | 250 | HV91 |
| CHL .386 .616 .265 .404 .261 .070 .379 .577 .035 | 824-3b | 450 | 334 | 330 | 330 | HV91 |
| CHL .490 .510 .229 .356 .045 .370 .314 .488 .185 | ch228 | 120 | 266 | 150 | 150 | HV91 |
| CHL .422 .577 .260 .292 .180 .267 .405 .454 .134 | ch139 | 240 | 310 | 250 | 250 | HV91 |
| CHL .413 .595 .052 .285 .229 .434 .119 .654 .217 | b12 | 210 | 321 | 270 | 270 | HV91 |
| CHL .411 .590 .038 .398 .206 .358 .072 .748 .179 | a3 | 210 | 318 | 270 | 270 | HV91 |
| CHL .435 .565 .318 .326 .136 .220 .437 .447 .110 | l19 | 235 | 302 | 270 | 270 | HV91 |
| CHL .260 .740 .056 .338 .491 .115 .134 .808 .058 | d16 | 480 | 415 | 270 | 270 | HV91 |

| **Sudoite-chloritoid-quartz**<br>**SUD $[Si\ Al]_{T2}[Mg\ Fe\ Al\ \square]_{M1}[Mg\ Fe\ Al]_{(M2+M3)}$**<br>**CLD $[Mg\ Fe]$** | | IV<br>T<br>°C | <br>P (fixed)<br>kb | |
|---|---|---|---|---|
| Lycian nappes | | | | |
| SUD .501 .498 .105 .028 .002 .869 .445 .120 .434 | Lyc11 | 343 | 4 | t.s. |
| CLD .189 .794 | | | | |
| SUD .505 .495 .069 .015 .000 .922 .440 .095 .461 | Lyc13 | 316 | 4 | t.s. |
| CLD .189 .794 | | | | |
| Peloponese | | | | |
| SUD .505 .495 .069 .015 .000 .922 .440 .095 .461 | Tg972-4/64 | 375 | 4 | t.s. |
| CLD .281 .719 | 65 | | | |
| SUD .492 .505 .066 .014 .012 .908 .447 .097 .454 | Tg972-4/67 | 397 | 4 | t.s. |
| CLD .345 .655 | 48 | | | |

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