

Energy calculations bearing on biopyriboles

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ABSTRACT

Energy calculations were used to evaluate the stability relationships for low Ca, low Al biopyribole polysomes in the compositional range defined by (010) pyroxene slabs (P slabs) with composition near $(\text{Mg,Fe})_4\text{Si}_4\text{O}_{12}$ and (010) mica slabs (M slabs) with composition near that of talc, $(\text{Mg,Fe})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. The calculations were performed using results of the structure refinements of two orthopyroxenes (Opx), clinoenstatite (Cpx), two amphiboles (anthophyllite = An, cummingtonite = Cu), chesterite (Ch), jimthompsonite (Jt), clinojimthompsonite, and talc (Tc). The energy calculations show the following. (1) For each intermediate polysome, the energy is lower than the energy of a compositionally equivalent assemblage of Tc + (Opx or Cpx). (2) Assemblages of Jt + Tc and Jt + (Opx or Cpx) have the lowest energies, all other assemblages being metastable. Thus the energy calculations indicate that Jt could be a stable phase. (3) The energetically permissible hydration reactions are generally consistent with reactions interpreted from textural observations. Only one kind of observed hydration reaction, (An or Cu) → Ch, could not be predicted from the energy calculations.

INTRODUCTION

Biopyriboles form an important polysomatic series. Individual structures in the series consist of (010) structure modules, M and P slabs, which are respectively like those of 2:1 mica [e.g., talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$] and pyroxene (e.g., enstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$) (Thompson, 1970, 1978; Veblen et al., 1977; Veblen and Burnham, 1978a, 1978b). The polysomatic model is particularly useful for understanding the crystal chemistry of real and hypothetical biopyriboles because intermediate biopyriboles, containing both M and P slabs, have properties that relate to the physical and chemical properties of the corresponding mica and pyroxene end-members. Atomic sites in a P slab retain nearly the same local environments that they would have in the end-member pyroxene. Likewise, atomic sites in an M slab retain nearly the same local environments as the corresponding sites in the end-member 2:1 phyllosilicate. Thus, cation site preference in a given polysome can be readily anticipated by analogy with site preferences in minerals corresponding respectively to the P and M slab parts of the polysome.

Perhaps the widest variety of natural biopyriboles are defined by P and M slabs having compositions respectively close to $(\text{Mg,Fe})_4\text{Si}_4\text{O}_{12}$, and $(\text{Mg,Fe})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. Enstatite and clinoenstatite would be examples of the . . . PPP . . . , or (P) polysome, where the parentheses enclose one cycle of the repeating sequence of M and P slabs. Talc would be the (M) polysome. The amphiboles, anthophyllite and cummingtonite, are the (MP) polysomes. Other naturally occurring polysomes in the same

compositional range include the (MMPMP) polysome chesterite, and two (MMP) polysomes, jimthompsonite and clinojimthompsonite (Veblen and Burnham, 1977a, 1978b). Chesterite contains both triple chains of Si tetrahedra (. . . PMMP . . .) and double chains (. . . PMP . . .). Jimthompsonite and clinojimthompsonite have only triple chains of Si tetrahedra.

Although it is well known that amphiboles are stable under appropriate conditions of *P*, *T*, and *a*(H_2O), it is not so clear that the relatively recently discovered chesterite, jimthompsonite, and clinojimthompsonite (Veblen and Burnham, 1978a, 1978b) necessarily crystallize as stable minerals. Certainly the relative obscurity of natural (MMPMP) and (MMP) polysomes, and occurrence as minute grains or lamellae in a host of pyroxene, amphibole, or mica, might suggest that they are metastable. Textural evidence (Veblen and Buseck, 1981) shows some systematic relationships involving the succession of polysomes during the progressive hydration of either pyroxene or an amphibole, but the reaction mechanisms are complex and remain poorly understood.

In an interesting analysis using the axial next-nearest-neighbor ising (ANNNI) model, Price and Yeomans (1986) show that jimthompsonite or clinojimthompsonite is very likely stable under appropriate conditions (*P*, *T*, composition), but chesterite is probably metastable under any conditions. The qualitative relationships indicate that the conditions for the stability of jimthompsonite or clinojimthompsonite should be fairly restricted.

In the present investigation, structure energy calculations were used to gain some insight into the relative

stabilities of the different polysomes in the pyroxene-talc polysomatic series. Specifically we set out to determine whether or not any of the polysomes, chesterite, jimthompsonite, and clinojimthompsonite could have a lower energy than compositionally equivalent assemblages of pyroxene + talc, or amphibole + talc.

The following abbreviations are used in this paper: orthopyroxene = Opx, clinopyroxene = Cpx, anthophyllite = An, cummingtonite = Cu, chesterite = Ch, jimthompsonite = Jt, clinojimthompsonite = cJt, and talc = Tc.

STRUCTURES

The energy calculations were limited by the availability of suitable structure determinations. Whereas structure determinations are available for a wide range of amphiboles (Hawthorne, 1983) and pyroxenes (Cameron and Papike, 1980), structure determinations are available for only three polysomes containing triple chains of Si tetrahedra, jimthompsonite, clinojimthompsonite, and chesterite (Veblen and Burnham, 1978a, 1978b), and for only two specimens of talc (Rayner and Brown, 1973; Perdakatsis and Burzlaff, 1981). Further complicating the analysis, the talc compositions are not strictly appropriate for a comparison with the M slabs in jimthompsonite, clinojimthompsonite, and chesterite. Like talc, the intermediate polysomes Ch, Jt, and cJt have only traces of Al and Ca; unlike talc, the Mg/(Fe + Mg) fractions in Ch, Jt, and cJt are in the range 0.70–0.78. Within these limitations, we sought low Ca, low Al structures with similar Mg/(Fe + Mg) ratios.

Pyroxene (P)

No one pyroxene structure, of those we considered (Cameron and Papike, 1980; Ohashi, 1984), had a satisfactory Mg/(Fe + Mg) ratio for comparison with Ch, Jt, and cJt. Consequently we used three structure determinations spanning the range of Mg/(Fe + Mg) in Ch, Jt, and cJt. The structures were of orthopyroxene [20 °C, Mg/(Fe + Mg) = 0.32] determined by Smyth (1973), synthetic orthoenstatite [Mg/(Fe + Mg) = 1] and synthetic clinoenstatite [Mg/(Fe + Mg) = 1], both determined by Ohashi (1984).

Amphiboles (MP)

For amphibole structures we used that of anthophyllite determined by Finger (1970, as reported in Hawthorne, 1973) and that of cummingtonite determined by Fisher (1966, as reported in Hawthorne, 1983). The Mg/(Fe + Mg) fractions in these minerals were 0.62 for the cummingtonite and 0.79 for the anthophyllite. The CaO content of the cummingtonite was 2.2 wt%, which translates to 0.35 Ca per 24 O atoms and is somewhat higher than would be desired for our purposes. The chemical analyses for anthophyllite reported no Ca. Ratios of ¹⁴¹Al/Si for both amphiboles were only slightly higher than the very low ¹⁴¹Al/Si ratios in chesterite, jimthompsonite, and clinojimthompsonite (Veblen and Burnham, 1978a).

Chesterite (MMP), jimthompsonite (MMPM), clinojimthompsonite (MMPM)

For these biopyriboles we used the only available structure determinations (Veblen and Burnham, 1978b).

Talc (M)

The Mg/(Fe + Mg) fraction is essentially 1 for the talc samples whose structures were refined by Rayner and Brown (1973) and Perdakatsis and Burzlaff (1981). By analogy with our energy calculations on orthopyroxene and orthoenstatite, the lack of a structure refinement for talc with a suitably comparable Mg/(Fe + Mg) fraction should not affect our conclusions. We used the more recent structure refinement of talc by Perdakatsis and Burzlaff (1981) primarily because the refinement provided an H site. Otherwise results of the refinement are not significantly different from those of Rayner and Brown (1973).

Talc crystallizes in space group *C1*, in such a way that the stacking of (001) unit layers (polytype *ITc*) is very different from the way in which comparable units are stacked in the M slabs of an intermediate biopyribole. The M slabs in cummingtonite have *C2/m* symmetry consistent with *IM* polytypic stacking, whereas the M slabs in anthophyllite have orthorhombic symmetry consistent with *2O* polytypic stacking. Therefore, in addition to calculating the energy of the observed talc-*ITc* structure, we calculated the energy for hypothetical *C2/m* talc-*IM*, which we fabricated from a unit layer of the observed talc-*ITc* structure. This was done in an effort to gain a better appreciation for the actual contribution by the M slabs to the cohesive energy of each intermediate biopyribole.

METHOD

Energy calculations were performed using the computer program WMIN (Busing, 1981). For a given structure, the program calculated the cohesive energy, given by

$$W_{\text{tot}} = \frac{1}{2} \sum_{i \neq j} \sum_j z_i z_j \epsilon^2 / r_{ij} + \frac{1}{2} \sum_{i \neq j} \sum_j \lambda_{ij} \exp(-r_{ij} / \rho_{ij}).$$

The first sum is the Coulomb electrostatic contribution, where z_i and z_j are formal valences on ions i and j , ϵ is electrostatic charge, and r_{ij} is the interionic separation. The summation is over all ions in the crystal, and the factor $1/2$ accounts for the fact that each interaction is included twice. The second term is the sum over short-range repulsive potentials, with coefficients λ_{ij} and ρ_{ij} characteristic of each interacting ion pair; summations are over all nearest neighbor cation-anion interactions and all nearest neighbor anion-anion interactions.

For Mg-O, Si-O, and O-O interactions, we employed short-range coefficients determined by Post and Burnham (1986) from modified electron-gas theory (MEG). Each O ion is surrounded with a spherical shell of charge +2 in the MEG procedure. The potential of the shell compensates for crystal field effects on the O charge density.

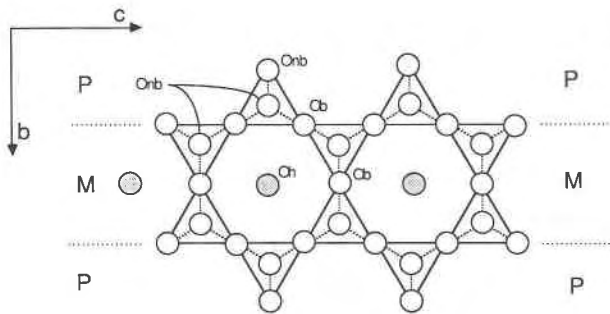


Fig. 1. Different kinds of O atoms in M and P slabs of a biopyribole. Ob = bridging O atom (Si-O-Si), Onb = nonbridging O atom (Si-O¹⁶M), and Oh = hydroxyl O atom.

The shell potential, V_{sh} ($= +2/r_{sh}$), is adjusted by varying the shell radius, r_{sh} . The short-range energy resulting from an O atom interacting with other ions (including other O ions), defined by λ and ρ , varies with shell potential. The appropriate shell radius for O atom yields a shell potential that is equal to the Coulomb potential at the O site in the crystal (Post and Burnham, 1986; Muhlhausen and Gordon, 1981a, 1981b).

All octahedral sites were considered to contain Mg^{2+} , since no Fe^{2+} -O short-range potentials are available. The presence of Fe^{2+} in a site will affect the calculated energy only to the extent that the polyhedral geometry is affected.

Energy calculations by one of us (C.W.B.), by Ohashi (1984), and by Smyth (1989) show that the O atoms of low Ca, low Al biopyriboles can be categorized conveniently by site potential as nonbridging P-module O atoms (Fig. 1) with $V = 1.83$ e/Å, bridging O atoms in either P or M modules with $V = 2.11$ e/Å, and nonbridging M-module O atoms or OH O atoms with $V = 1.98$ e/Å. Appropriate shell radii for the three types are 1.09 Å, 0.95 Å, and 1.01 Å, respectively; values for λ and ρ were selected accordingly from data given by Post and Burnham (1986).

TABLE 1. Calculated H positions

Polysome	Site	x	y	z	H-O (Å)
Anthophyllite	Ha	0.23345	0.25000	0.56023	0.9514
	Hb	0.01768	0.25000	0.22827	0.9599
Cumingtonite	H	0.21581	0.0	0.74267	0.9530
Chesterite	Hta	0.23503	0.30035	0.31540	0.9598
	Htb	0.51791	0.30106	0.01271	0.9609
	Hda	0.26762	0.49956	0.81022	0.9511
	Hdb	0.48524	0.50036	0.47464	0.9596
Jimthompsonite	Ha	0.23467	0.33543	0.06311	0.9571
	Hb	0.51700	0.33519	0.76679	0.9614
Clinojimthompsonite	H	0.21809	0.08539	0.22207	0.9570
Talc-1Tc	H	0.72532	0.66862	0.21525	0.9599
(observed values)		(0.719)	(0.669)	(0.203)	(0.84)
Talc-1M	H	0.69845	0.70238	0.21519	0.9593

Note: H coordinates refer to structure determinations as follows: anthophyllite (Finger, 1970); cumingtonite (Fisher, 1966); chesterite, jimthompsonite, clinojimthompsonite (Veblen and Burnham, 1978b); talc-1Tc (Perdakatsis and Burzlaff, 1981); talc-1M (this study; structure parameters can be obtained from authors).

TABLE 2. Calculated dissociation energies

Polysome	D_o (kJ/mol of O)	Structure determination
Orthoenstatite	-4635	Ohashi, 1984
Clinoenstatite	-4634	Ohashi, 1984
Orthopyroxene (20 °C)	-4635	Smyth, 1973
Anthophyllite	-4631	Finger, 1970
Cumingtonite	-4632	Fisher, 1966
Chesterite	-4625	Veblen and Burnham, 1978b
Jimthompsonite	-4634	Veblen and Burnham, 1978b
Clinojimthompsonite	-4631	Veblen and Burnham, 1978b
Talc-1Tc	-4616	Perdakatsis and Burzlaff, 1981
Talc-1M	-4610	This study

Treatment of H in the various polysomes containing M modules posed two special problems. Short-range H-O potentials cannot be obtained from MEG theory, and observed H positions are available only for talc (Perdakatsis and Burzlaff, 1981). With regard to the first problem, for O-H interactions we used an empirical short-range potential from Abbott et al. (1989). With regard to the second problem, it was necessary to calculate hypothetical H^{1+} positions for all of the intermediate polysomes. The procedure involved a search, using WMIN, for the H position(s) of lowest energy. During the search, the positions of all other atoms were fixed. Table 1 gives the calculated H positions. We also calculated a hypothetical H position for talc-1Tc, which may be compared with the observed position (Perdakatsis and Burzlaff, 1981). In talc-1Tc, the OH dipole orientation for the calculated H site is nearly perpendicular to (001), consistent with the observed orientation. However, because the observed H-O distance in talc seems to be questionably short (0.84 Å), and for the sake of internal consistency, in subsequent energy calculations on talc-1Tc we used the calculated, hypothetical H position. In anthophyllite and cumingtonite the calculated O-H distances and OH orientations, nearly perpendicular to (100), are consistent with observed relationships in tremolite (Hawthorne and Grundy, 1976).

The calculated cohesive energies (Table 2) include self-energy terms for O ions. These terms represent the energy difference between free ions and shell-stabilized ions. The self-energy terms also include the energy for the reaction $O^{2-} \rightarrow O^{1-} + e$, since O^{2-} is unstable as a free ion (Post and Burnham, 1986).

RESULTS

The calculated dissociation energies (Table 2) are represented graphically in Figure 2. Assuming the structures are correct, the dissociation energies would be exact (within the limits of computing precision), except for uncertainties in the shell radii of the different kinds of O atoms. If the shell radius for a particular kind of O atom is changed by a small amount (e.g., +2% for an Onb-O atom in enstatite the effect on the calculated dissociation energy is small (+3.5kJ/anion for enstatite; i.e., < +0.1%),

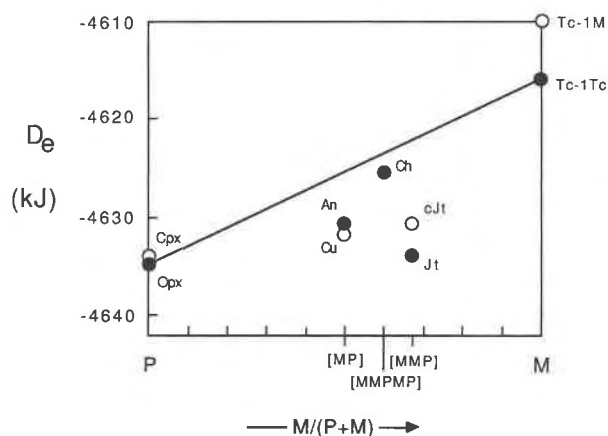


Fig. 2. Calculated energies (kJ/mol of O) of the different polysomes, plotted against fraction $M/(P + M)$ of (010) M and P slabs. Abbreviations: Opx = orthopyroxene, Cpx = clinopyroxene, An = anthophyllite, Cu = cummingtonite, Ch = chessterite, Jt = jimthompsonite, cJt = clinojimthompsonite, and Tc = talc.

but more importantly, across the polysomatic series the effect is proportional to the $M/(P + M)$ fraction. In Figure 2, this means that the slope of the line connecting the dissociation energies of enstatite and talc-1Tc could be slightly more or less steep and translated up or down a small amount, but the energies for the other polysomes would be distributed in the same way relative to the enstatite-talc line. Hence, the quantitative aspects of the results are relatively insensitive to small uncertainties in the shell radii of the O atoms, whereas the more important qualitative aspects are for practical purposes insensitive to the uncertainties.

Energies for the three varieties of pyroxene are nearly the same (Table 2, Fig. 2). Thus, at least within the limitations of the present approach, Fe-Mg exchange would seem to have little influence on the dissociation energy. As expected, the difference in the energies of monoclinic and orthorhombic polymorphs at specific polysomatic M/P ratios (i.e., pairs Opx-Cpx, An-Cu, or Jt-cJt) is very small, in general significantly smaller than the energy differences between polysomes with different M/P ratios.

It is perhaps worth noting that our hypothetical talc-1M has a significantly higher energy than natural talc-1Tc. The 1M configuration of the M slabs in clinopyroxene and clinojimthompsonite, and 2O configuration of the M slabs in orthopyroxene, jimthompsonite, and chessterite must be stabilized at least in part by adjacent P slabs. As self-evident as this point may seem, the high energy of the hypothetical talc-1M suggests furthermore that there may be a natural limit to the width of chains of Si tetrahedra in intermediate polysomes—a limit (perhaps triple chains) beyond which the structure would otherwise tend to disrupt into discrete domains of talc-1Tc and a double or triple chain polysome.

Other important results are as follows:

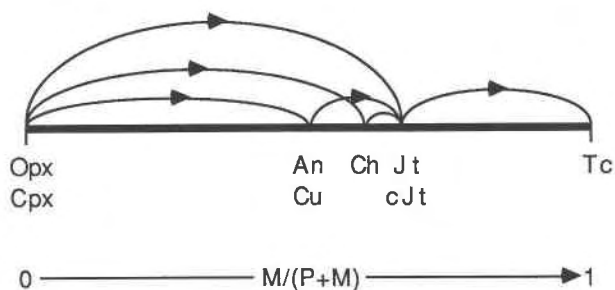


Fig. 3. Schematic representation of permissible hydration reactions for polysomes on the pyroxene-talc join.

1. Each of the polysomes, An, Cu, Ch, Jt, and cJt, has a lower energy than a compositionally equivalent mixture of Opx + Tc or Cpx + Tc. During hydration, the replacement of Opx or Cpx by any one of the intermediate polysomes would be energetically favorable inasmuch as the energy of the product would be lower than the energy of a compositionally equivalent assemblage of Opx + Tc or Cpx + Tc. We will refer to such favorable replacement reactions as permissible. With regard to Opx and Cpx the permissible reactions include Opx \rightarrow An or Cpx \rightarrow An, Opx \rightarrow Cu or Cpx \rightarrow Cu, Opx \rightarrow Jt or Cpx \rightarrow Jt, Opx \rightarrow cJt or Cpx \rightarrow cJt, and Opx \rightarrow Ch or Cpx \rightarrow Ch.

2. The phases cJt and Jt each have a lower energy than a mechanical mixture of An + Tc or Cu + Tc; thus the permissible hydration reactions are An \rightarrow cJt or Cu \rightarrow cJt and An \rightarrow Jt or Cu \rightarrow Jt.

3. The phases cJt and Jt each have lower energies than a mechanical mixture of Ch + Tc, thus two more permissible reactions are Ch \rightarrow cJt and Ch \rightarrow Jt.

4. Any mechanical mixture of Jt + Tc has a lower energy than a compositionally equivalent mixture of Tc and any other polysome; thus the final permissible reaction is Jt \rightarrow Tc. Energies for mixtures of cJt + Tc are not much higher than those of compositionally equivalent mixtures of Jt + Tc. Except for assemblages of Jt + Tc, mixtures of cJt + Tc have lower energies than compositionally equivalent mixtures of Tc and any other polysome. Thus, except for the polymorphic transformation cJt \rightarrow Jt, the reaction cJt \rightarrow Tc would be permissible.

Figure 3 summarizes the permissible reactions just described. For simplicity we have omitted reactions to talc that may be energetically favorable, but produce mixtures that have higher energies than chemically equivalent mixtures of Jt + Tc. The relationships compare favorably with the petrographic observations of Veblen and Buseck (1981), specifically their Figure 28. Only one important replacement, (Cu or An) \rightarrow Ch, is not supported by the calculated energies. The calculations suggest that the stable assemblages are Jt + Opx and Jt + Tc, all other assemblages being metastable.

CONCLUSIONS

1. Using the method of Abbott et al. (1989), realistic H positions can be calculated for biopyriforms.

2. For each intermediate polysome, the energy is lower than the energy of a compositionally equivalent mixture of pyroxene and talc.

3. The energetically permissible hydration reactions are generally consistent with reactions interpreted from textural observations. Only one kind of observed hydration reaction, amphibole \rightarrow chesterite, could not be predicted from the energy calculations. These relationships are consistent with the ANNNI model (Price and Yeomans, 1986), which indicates that jimthompsonite or clinojimthompsonite may be stable, but chesterite is most likely metastable.

Our results demonstrate a relatively simple and practical application of energy calculations to the interpretation of phase relationships. We believe that the method may be equally useful in other systems.

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