

Crystal chemistry of a Mg-vesuvianite and implications of phase equilibria in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ ¹

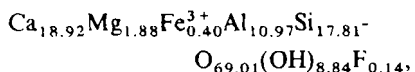
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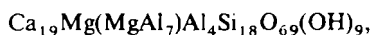
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Abstract. Chemical analysis (including H_2 , F_2 , FeO , Fe_2O_3) of a Mg-vesuvianite from Georgetown, Calif., USA, yields a formula,



in good agreement on a cation basis with the analysis reported by Pabst (1936). X-ray and electron diffraction reveal sharp reflections violating the space group P4/nnc as consistent with domains having space groups P4/n and P4nc. Refinement of the average crystal structure in space group P4/nnc is consistent with occupancy of the A site with Al, of the half-occupied B site by 0.8 Mg and 0.2 Fe, of the half-occupied C site by Ca, of the Ca (1, 2, 3) sites by Ca, and the OH and O(10) sites by OH and O. We infer an idealized formula for Mg-vesuvianite to be



which is related to Fe^{3+} -vesuvianite by the substitutions $\text{Mg} + \text{OH} = \text{Fe}^{3+} + \text{O}$ in the B and O(10) sites and $\text{Fe}^{3+} = \text{Al}$ in the AlFe site.

Thermodynamic calculations using this formula for Mg-vesuvianite are consistent with the phase equilibria of Hochella, Liou, Keskinen & Kim (1982) but inconsistent with those of Olesch (1978). Further work is needed in determining the composition and entropy of synthetic *vs* natural vesuvianite before quantitative phase equilibria can be dependably generated. A qualitative analysis of reactions in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ shows that assemblages with Mg-vesuvianite are stable to high T in the

absence of quartz and require water-rich conditions ($\text{XH}_2\text{O} > 0.8$). In the presence of wollastonite, Mg-vesuvianite requires very water-rich conditions ($\text{XH}_2\text{O} > 0.97$).

Key-words: petrogenetic grid; vesuvianite

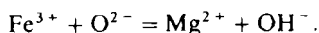
INTRODUCTION

Vesuvianite (idocrase) is an important rock-forming mineral in calc-silicate rocks equilibrated under a wide range of metamorphic pressures and temperatures. Vesuvianite is most commonly reported in contact metamorphic aureoles formed at pressures of less than 2 kbar (e.g. Burnham, 1959; Kerrick, Crawford & Randazzo, 1973; Joesten, 1974), but higher pressure occurrences are from greenschist (Braitsch & Chatterjee, 1963), amphibolite (Trommsdorff, 1968; Kohl, 1976), and occasionally even granulite facies rocks (Palache, 1935; Tracy, Jaffe & Robinson, 1978; Valley & Essene, 1979). Vesuvianite also occurs in rodingites (e.g. Baltatzis, 1984) and nepheline syenites (Deer, Howie & Zussman, 1962).

Many metamorphic reactions and petrogenetic grids have been proposed for vesuvianite, but their calibration has been seriously hampered by the lack of equilibrium experiments and by uncertainties in the crystal structure and chemical formula of vesuvianite. Analyses of vesuvianite from granulite facies marbles in the Adirondack Mountains (Valley & Essene, 1979) indicated that the vesuvianite was Mg-rich, requiring charge balancing by hydroxyl ion in excess of that apparently permitted by some previously proposed formulae. Without an accurate formula, chemical reactions could not be adequately evaluated.

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We have therefore carried out a refinement of the structure of a vesuvianite from Georgetown, California (Pabst, 1936) in order to better define the composition relations. This sample approaches the natural end-member Mg-vesuvianite composition. Because Fe-vesuvianite contains iron dominantly in the ferric state (Deer *et al.*, 1962), the Mg^{2+} substitution for Fe^{3+} requires a coupled substitution such as:



This substitution suggests that there will be additional hydroxyl in Mg-vesuvianite relative to Fe-vesuvianite. The OH content of vesuvianite is significant, because vesuvianite breaks down by dehydration reactions, and the quantity of derived volatiles controls the slope and placement reactions in P-T and T-X(H_2O - CO_2) space. In this study we have determined the probable structural sites for Mg^{2+} relative to Fe^{3+} and have confirmed the distribution of OH. We have used a well-constrained formula for Mg-vesuvianite to evaluate experimental equilibria on the stability of vesuvianite + quartz (Olesch, 1978; Hochella, Liou, Keskinen & Kim, 1982).

CHEMICAL ANALYSIS

A specimen of white vesuvianite from Georgetown, Calif., USA (Pabst, 1936) was kindly

provided to us by Dr A. Pabst. The composition of the specific material under study was analysed (J.W.V.) using an electron microprobe (Table 1). The conditions of the analysis are the same as those of Valley & Essene (1980). The original analysis reported by Pabst (1936) shows good agreement for most cations (Table 1). The FeO and H_2O were determined by wet chemical analyses (J.R.B. and J.W.V.). Two separate determinations yielded values of 0.10 and 0.00 wt% FeO with an average value of 0.05 wt%. Hydrogen was determined by thermal decomposition at 1500°C for 15 min. Evolved gases were quantitatively converted to H_2 by reaction with uranium metal at 700°C, and H_2 was measured volumetrically. This technique is standard for hydrogen isotope analyses and has been shown to be accurate by analyses of micas and amphiboles where stoichiometry and composition (including F and Cl) are known (Bowman, 1978). The H_2 evolved from 100 mg of this vesuvianite is equivalent to 2.77 wt% H_2O . This is much higher than the 0.70 wt% obtained by Herdsman (Pabst, 1936), presumably because of Herdsman's partial extraction of H_2O at lower temperatures. The value for hydroxyl appears to be somewhat high relative to the formula proposed by Rucklidge, Hemingway & Fisher (1979) on the basis of crystal structure refinements.

Table 1. Chemical analyses of Mg-vesuvianite, Georgetown, California, USA

	Oxide (wt%)			Moles per 50 cations		
	Pabst (1936)	Our data		Pabst (1936)	Our data	Site
SiO_2	37.70	37.23	Si	17.77	17.81	Si(1, 2, 3)
TiO_2	tr	<0.05	Al	0.23	0.19	
Al_2O_3	19.30	19.46	Al	4.00	4.00	A
Fe_2O_3	0.85	1.10*	Al	6.49	6.78	AlFe†
FeO	0.37	0.05	Fe^{3+}	0.12	0.21	
MnO	tr	<0.05	Fe^{2+}	0.15	0.02	
MgO	2.45	2.64	Mg	0.91	1.07	B‡
CaO	38.30	36.92	Mg	0.81	0.81	
Na_2O	nil	<0.05	Fe^{3+}	0.19	0.19	
K_2O	n.a. §	<0.05	Ca	1.00	1.00	C
H_2O^*	0.70	2.77*	Ca	18.34	17.92	Ca(1, 2, 3)
CO_2	nil	n.a. §	OH	2.83	8.84	OH and O(10)
F_2	nil	0.09	F	nil	0.14	
Sum	99.67	100.22	O	7.17	1.02	
			O	67.54	67.99	O(1-9)
Density	3.322 (meas.)	3.367 (calc.)				

* Measured directly as described in text.

† Remaining Mg, Fe^{2+} , Fe^{3+} assigned to AlFe site.

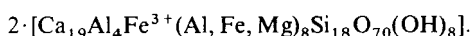
‡ Mg and Fe^{3+} assigned to B site in agreement with refined cell occupancies.

§ n.a. = not analysed.

¶ Adjusted for $\text{O} \equiv \text{F}$.

CRYSTAL STRUCTURE ANALYSIS

The vesuvianite structure was originally solved by Warren & Modell (1931). The basic features of this structure as consistent with space group P4/nnc were largely confirmed by Coda, Della Giusta, Isetti & Mazzi (1970) and Rucklidge *et al.* (1979) who obtained results modifying those of Warren & Modell. Giusepetti & Mazzi (1983) subsequently refined the structure of a specimen which has space group P4/n. Rucklidge *et al.* implied that vesuvianite has the formula:

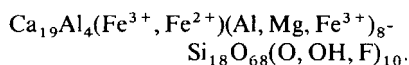


This formula will balance if the AlFe site has $R^{2+}/R^{3+} = 1/7$ and places an upper limit of one Mg atom per fifty cations in vesuvianites that are Na-, Ti-, Be-, or rare earth-free. This structure has 38 Ca with eightfold coordination in four different equipoints [C, Ca(1), Ca(2), Ca(3)] with Ca-O distances and polyhedral geometries with which only Ca is compatible, considering the elements commonly found in vesuvianite. (Tables 1 and 4 collectively list data on equipoint nomenclature, rank, and occupancy.) The A site contains only 4 Al in irregular octahedral coordination. There is significant solid solution of octahedrally coordinated cations only in the more irregularly coordinated AlFe site of rank 8, to which Ti, Mn and Mg are also assigned. The B site, having an unusual square pyramidal coordination, is assumed to be occupied only by Fe³⁺ and Mg. A critical feature is that C and B sites alternate parallel to the *c*-axis, with such short interatomic distances that occupancy of only one half of each site is possible. There are therefore four vacant and 100 occupied cation sites.

The cation polyhedra impose severe restrictions on the chemistry of the various sites in vesuvianite. However, a complicating factor is the presence of reflections which violate the glide plane extinctions of space group P4/nnc (Arem & Burnham, 1969). These reflections are not observed in all single-crystal photographs of vesuvianite. Rucklidge *et al.*, (1979) noted that such reflections could be caused by ordering of B and C occupancies along the *c*-axis, resulting in a space group which is a subgroup of P4/nnc. Indeed, Allen & Burnham (1983) noted that vesuvianite which displays the reflections violating space group P4/nnc is acentric.

Giusepetti & Mazzi (1983) confirmed that ordering of the B and C cations and vacancies along the *c*-axis results in a symmetry which is a subgroup of P4/nnc. As a result of a survey of several vesuvianites, they showed that either of

two ordering schemes may occur, consistent with space groups P4/n and P4nc, respectively. As these space groups have different extinction rules relative to space group P4/nnc, a crystal having domains with only one ordering scheme may be identified. Giusepetti & Mazzi (1983) showed that vesuvianite from Val d'Ala (Piemonte, Italy) has space group P4/n; they refined the structure and confirmed that Ca and Fe are ordered relative to vacancies along the *c*-axis. They showed that their vesuvianite has the formula:



Single crystals of the specimen provided by Pabst were studied using conventional Weissenberg and precession techniques. The photographs showed the presence of sharp reflections violating the *n*- and *c*-glide extinction rules, as noted by Arem & Burnham (1969) in specimens from other localities. In addition, intensities of selected hk0 and kh0 reflections were determined using a single-crystal diffractometer and determined to be equal within error of observation, as required by space group P4nc. However, hk0 reflections with *h* + *k* odd were relatively weak, while h0l reflections with *h* + 1 odd, and hhl reflections with *l* odd were relatively intense. As shown by Giusepetti & Mazzi (1983), this indicates that our material possesses a cation ordering scheme primarily consistent with space group P4/n, but with domains having space group P4nc. The apparent equivalence of kh0 and hk0 intensities must have been inferred on the basis of too small and selective a choice of reflections.

To investigate relations between domains related by different ordering schemes, or to determine the presence of possible twinning, an oriented, ion-thinned single-crystal was examined using a JEOL-JEM 100CX electron microscope. h0l reflections were observed to be intense and sharp, as consistent with space group P4/n. Furthermore, they were constant in relative intensity over the entire electron-transparent area of the specimen. This is in contrast to the results of Allen & Burnham (1983), who observed that the relative intensities of these reflections waxed and waned as the area under study was varied in at least one specimen. Imaging in both bright and dark field modes failed to produce contrast indicative of a domain structure. Because the X-ray diffraction results are consistent with the existence of domains having two different space groups, the TEM results imply that such domains have sizes below the level of resolution of these

data (approximately 100 Å) or that the area sampled by TEM was homogeneous by chance.

We had used space group P4/nnc for our refinement. Subsequent to our investigation, Giusepetti & Mazzi (1983) determined the true symmetry relations and defined the cation-vacancy ordering scheme for a crystal with space group P4/n. Based on their analysis, our vesuvianite has

Table 2. X-ray powder diffractometer data for Mg-vesuvianite

I/I ₀	d _{obs}	d _{calc}	hkl
5	11.0	10.97	110
7	5.93	5.98	211*
17	5.88	5.90	002*
3	5.49	5.49	220*
7	4.68	4.70	202*
7	4.02	{ 4.04	321
		{ 4.02	222
2	3.88	3.88	400
14	3.47	{ 3.48	322
		{ 3.47	420
12	3.24	3.24	402
2	3.15	{ 3.17	412
		{ 3.13	303
8	3.067	3.068	313*
12	3.043	3.042	510*
14	2.995	{ 3.001	431
		{ 3.001	501
		{ 2.990	422
100	2.938	2.450	004
		2.946	511
5	2.902	2.903	323*
7	2.849	2.849	114*
100	2.748	{ 2.751	204
		{ 2.746	432
		{ 2.742	440
10	2.655	2.661	530*
70	2.597	{ 2.602	423
		{ 2.598	224
		{ 2.596	531
4	2.525	2.528	314*
6	2.487	{ 2.493	611
		{ 2.487	442
50	2.454	2.453	620*
8	2.421	2.425	532*
5	2.369	{ 2.373	541
		{ 2.368	602
8	2.345	{ 2.348	404
		{ 2.341	612
9	2.325	{ 2.333	523
		{ 2.324	414
5	2.296	2.296	334
12	2.205	2.204	533
4	2.194	{ 2.194	710
		{ 2.194	550
5	2.178	2.178	701
18	2.155	{ 2.157	711
		{ 2.153	632

* Reflections used in lattice parameter refinement.

domains having two different ordering schemes and the refined structure is an average one. Data for a refinement could not be obtained from a crystal having a single ordering scheme. We have therefore chosen to report these results, whose significance is primarily in the determination of composition relations, for the average structure.

Lattice parameters were determined to be $a = 15.513(8)$ and $c = 11.800(6)$ Å by least-squares refinement of internally standardized powder diffractometer data (Table 2). A crystal mounted along the c -axis and measuring $0.15 \times 0.20 \times 0.23$ mm was mounted on a Supper-Pace automated diffractometer using MoK $_{\alpha}$ radiation monochromated with a flat graphite crystal to measure the intensities of 1645 reflections having $h \geq k$, as consistent with Laue symmetry $4/m2/m2/m$, and $\sin \theta \leq 0.46$. The intensities were corrected for Lorentz, polarization and absorption factors ($\mu_1 = 24.5 \text{ cm}^{-1}$) using a modified version of the program ABSORP written by C. W. Burnham.

Refinement was carried out utilizing the program RFINE2 (Finger & Prince, 1975). Scattering factors were those of Doyle & Turner (1968) and the weighting scheme was that of Cruickshank (1965, p. 114). Refinement of coordinates proceeded normally, starting with the coordinates of Rucklidge *et al.* (1975), and assuming occupancy of sites A, AlFe, B, and C by Al, Al, Mg, and Ca, respectively. Near the final stages of refinement the isotropic temperature factors and the occupancy factors of these sites were allowed to vary, yielding the occupancies given in Table 3. A difference Fourier synthesis was calculated to determine the nature of average deviations of the structure from the average space group symmetry P4/nnc. This contained no significant features and the refinement was therefore terminated. The final conventional R-factor is 10.4%, excluding unobserved reflections and those that violate the extinction rules. Structure factors are available from D.R.P. upon request, atom parameters are listed in Table 4, and selected interatomic distances in Table 5.

Table 3. Refined occupancy factors

C	Ca	0.59(6)
	Mg	-0.09
B	Mg	0.41(3)
	Fe	0.095
AlFe	Al	1.05(1)
	Fe	-0.05
A	Al	1.04(2)
	Fe	-0.04

Table 4. Refined atom coordinates and isotropic temperature factors

Atom	Equipoint rank	X	Y	Z	B(A ²)
Si(1)	4	3/4	1/4	0	1.05(9)
Si(2)	16	0.8194(2)	0.0410(2)	0.8710(3)	0.80(6)
Si(3)	16	0.9160(2)	0.8490(2)	0.3646(3)	0.98(6)
Ca(1)	4	3/4	1/4	1/4	1.02(7)
Ca(2)	16	0.8105(1)	0.0444(1)	0.3794(2)	1.00(5)
Ca(3)	16	0.8984(1)	0.8177(1)	0.8873(2)	1.23(3)
C	4	3/4	3/4	0.1507(8)	1.27(13)
B	4	3/4	3/4	0.0292(10)	0.57(15)
AlFe	16	0.8877(2)	0.1216(2)	0.1216(3)	0.86(6)
A	8	0	0	0	0.65(7)
O(1)	16	0.7795(4)	0.1724(5)	0.0862(7)	1.06(12)
O(2)	16	0.8830(4)	0.1596(4)	0.2776(7)	0.91(11)
O(3)	16	0.9515(4)	0.2220(4)	0.0760(6)	0.78(12)
O(4)	16	0.9388(4)	0.1063(5)	0.4690(7)	1.08(12)
O(5)	16	0.8290(5)	0.0137(5)	0.1772(8)	1.55(13)
O(6)	16	0.8786(5)	0.7285(5)	0.0583(8)	1.78(15)
O(7)	16	0.0555(5)	0.1718(5)	0.3230(7)	1.34(13)
O(8)	16	0.9382(5)	0.9098(5)	0.0650(7)	1.19(13)
O(9)	8	0.8546(5)	0.8546	1/4	1.41(17)
O(10)	4	3/4	3/4	0.8676(14)	1.54(27)
OH	16	0.9958(5)	0.0612(5)	0.1378(7)	1.28(13)

INTERPRETATION OF CRYSTAL CHEMISTRY

We are principally concerned with an understanding of the chemical data in relation to the refined structure for Mg-vesuvianite. As a starting point for the crystal-chemical interpretations, we normalized the analysis to 50 cations (Table 1), one half of the total number of cations per unit cell. Normalizing to individual cation sites is not possible, a priori, due to the possibility of solid solution in each site. The final site assignments were made using X-ray refined values for Fe and Mg on the B site. It is interesting to note that the calculated Mg and Fe³⁺ partition approximately equally between the B and AlFe sites, although analytical and refinement errors make any calculation of intrasite partitioning uncertain. Although normalizing to the number of anions is possible in our case, as data for the Fe²⁺/Fe³⁺ and H content are available, such a process is judged to be somewhat less accurate than normalizing to cations. We recommend normalization to 50 cations as a general rule for vesuvianite formulae.

The sites Ca(1), Ca(2), Ca(3), and C have eight-fold coordinations consistent with occupancy only by Ca. The number of Ca atoms is 37.85 per 100 cations. The ranks of the equipoints sum to 38 (with half occupancy for site C), and therefore the analysis and symmetry constraints agree, within

error. 0.38 atom is required to complete the occupancy of the tetrahedral sites (which total 36 cations per cell). The average T-O distances for Si(1) and Si(2) are slightly greater than for Si(3). However, the differences are so small that it is not possible to unambiguously determine which sites are occupied by the small amount of the tetrahedrally coordinated Al.

The A and AlFe sites of vesuvianite have refined occupancies and bond distances (average M-O distances are 1.895 and 1.957 Å, respectively) consistent with occupancy only by Al and Mg, the scattering factors for which are nearly equal. The M-O distances are only slightly greater than those of Rucklidge *et al.* (1979, 1.892 and 1.951, respectively), although their occupancy values indicated the presence of significant Fe on the AlFe site. Because the M-O distances for our refinement are greater for that site, and approximately 0.5 Fe atoms (see discussion of B site below) are required to complete octahedral occupancy, we assume that the extra Fe is accommodated there. This requires that the AlFe occupancy value be in error by approximately 0.06, which is not unreasonable for an average structure.

The O(10), B and C sites (see fig. 2b of Rucklidge *et al.* (1979) for details of these sites) lie along a four-fold axis in the order O(10)-B-C-O(10). Alternate B and C sites are so close as to permit occupancy only by either B or C. The

Table 5. Selected interatomic distances

Si(1)	40(1)	1.640(8)
Si(2)	0(2)	1.647(7)
	0(3)	1.641(7)
	0(4)	1.662(8)
	0(7)	1.608(8)
	ave.	1.640
Si(3)	0(5)	1.624(8)
	0(6)	1.615(9)
	0(8)	1.617(8)
	0(9)	1.656(5)
	ave.	1.628
Ca(1)	40(1)	2.323(8)
	40(2)	2.515(7)
	ave.	2.419
Ca(2)	0(1)	2.461(7)
	0(2)	2.429(7)
	0(3)	2.374(8)
	0(4)	2.449(8)
	0(5)	2.451(9)
	0(5)'	2.315(8)
	0(6)	2.962(9)
	0(8)	2.349(7)
	ave.	2.474
Ca(3)	0(3)	2.447(7)
	0(6)	2.466(10)
	0(7)	2.588(9)
	0(7)'	2.492(8)
	0(7)''	2.373(8)
	0(8)	2.611(8)
	0(10)	2.541(3)
	OH	2.512(8)
	ave.	2.504
C	40(6)	2.298(10)
	40(9)	2.576(7)
	ave.	2.437
B	40(6)	2.052(8)
	0(10)	1.908(19)
	ave.	2.023
AlFe	0(1)	1.914(8)
	0(2)	1.884(8)
	0(3)	1.938(8)
	0(4)	2.080(8)
	0(5)	1.997(9)
	OH	1.927(8)
	ave.	1.957
A	20(4)	1.938(7)
	20(8)	1.862(7)
	20H	1.885(8)
	ave.	1.895

refinement is consistent with half occupancy for each site with approximately 80% of the B site occupied by Mg (or Al) and 20% by Fe. This site was shown by Rucklidge *et al.* (1979) and Giusepetti & Mazzi (1983) to be primarily occupied by Fe which is probably in the ferric state.

The refined occupancy factor for the B site is consistent with occupancy either by Mg or Al as they have nearly identical scattering powers. However, the average B–O distances (2.02 Å) gives some indication of the occupancy, where the B site has fivefold square pyramidal coordination. The effective ionic radii (Shannon & Prewitt, 1969) imply cation–oxygen distances for the relevant fivefold coordinated ions of 2.06 (Mg^V), 1.88 (Al^V) and 1.98 Å ([Fe³⁺]^V). The value for Mg is similar to our observed value (2.02 Å), especially when corrected for 20% substitution of Fe³⁺, while that for Al is very different. By comparison, the value for the M(3)A site of Giusepetti & Mazzi (1983) is 1.975 Å, compatible with Fe³⁺ in the B-site of their structure. The apparent evidence for Mg occupancy of the B site in Mg-vesuvianite is tempered by two factors: (1) the predicted Mg–O and Al–O distances are relatively imprecise, and (2) the B–O distance is the average for a half-occupied site and a half-unoccupied site. As Giusepetti & Mazzi (1983) showed, the unoccupied site is larger than the occupied Fe³⁺ site. Nevertheless, the evidence does imply occupancy of the B site by Mg in Mg-vesuvianite, and we tentatively conclude that the principal solid solution in that site involves Fe³⁺ and Mg. F. M. Allen and C. W. Burnham (personal communication, 1984) have found that the B site may also be occupied by Fe²⁺, on the basis of Mossbauer studies. That is consistent with our assignment of divalent Mg rather than Al to that site. However, in our sample there are only trace amounts of Fe²⁺ so that its possible effect on the B site need not be considered.

The atom O(10) plays a critical role in the structure of vesuvianite. It completes a square pyramidal coordination for the B site. It is also coordinated by 4Ca(3) atoms with Ca–O(10) = 2.53 Å. Coda *et al.* (1970) hypothesized that a hydrogen atom is associated with O(10) and Giusepetti & Mazzi (1983) conclude that there is a hydrogen bond between two adjacent O(10) atoms.

Using the measured value for Fe³⁺, we calculate that there must be 137.95 O²⁻ and 17.97 (OH, F) per unit cell (assuming 100 cations). This yields 155.92 anions, in excellent agreement with the theoretical value of 156. This in turn requires

that the O(10) site is occupied by 1.77 OH, 0.27 F and 1.96 O, and that the total of H₂O must be 2.79 wt %, including the OH in the OH site. This corresponds to the direct analysis for H₂O of 2.77%, in remarkable agreement with 50% occupancy of O(10) by OH and F and 50% by O. As shown by Giusepette & Mazzi (1983), in the ordered structure, O(10) is divided into two sites, O(10)A and O(10)B, which have a separation of 2.75. As the ordering requires valence sums of approximately +1.0 and +1.5 to O(10)A and O(10)B, respectively, there is a strong implication that a maximum of a single hydrogen atom may be associated with these atoms. Thus the limiting composition of vesuvianite may correspond to 9(OH, F), consistent with the composition of our sample.

Our data, when combined with that of Coda *et al.* (1970), Rucklidge *et al.* (1979) and Giusepette & Mazzi (1983) imply the following end-member chemistries for the B and O(10) sites (per 100 cations):

- (1) Fe₂³⁺O₄
- (2) Mg₂(OH)₂O₂.

Thus, there is strong evidence that common Fe-Mg vesuvianites are related by the coupled substitution Mg + OH = Fe³⁺ + O, although Fe²⁺ may also substitute in the B site in some cases. It is uncertain whether or not the O(10)

site may be more than half-occupied by OH. Additional Fe may replace Al in the AlFe site as indicated by the many Fe-vesuvianite analyses which contain Fe in excess of one atom per fifty cations (e.g., Deer *et al.*, 1962; Rucklidge *et al.*, 1979; Dobson, 1982; Harris & Einaudi, 1982; Meinert, 1982).

We conclude that Mg-rich vesuvianite has a chemistry which is compatible with the average structures of Coda *et al.* (1970) and Rucklidge *et al.* (1975) and the ordered structure of Giusepette & Mazzi (1983). If analyses are normalized to fifty cations per half-unit cell, the seemingly complex results may be interpreted in a relatively straightforward manner. The now-established formula for Mg-vesuvianite permits evaluation of its phase equilibria in the system CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂.

EXPERIMENTS ON THE STABILITY OF VESUVIANITE

Ito & Arem (1970, 1971), Shoji (1971, 1975), Olesch (1978), and Hochella *et al.* (1982) report experiments on the quartz-absent upper stability of Mg-vesuvianite by its decomposition to melilite, wollastonite, monticellite, and/or clinopyroxene. The earlier workers give synthesis boundaries rather than experimental reversals, and their phase equilibria are therefore not well constrained.

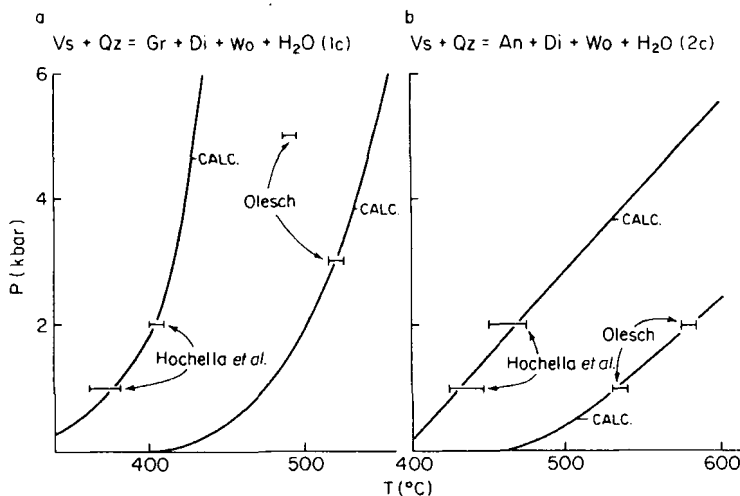
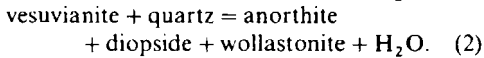
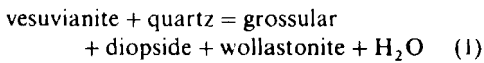


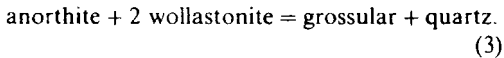
Fig. 1. Reactions 1 and 2 calculated using Mg-vesuvianite formula *Vs(c)* (this study) and compared with experiments of Olesch (1978) and of Hochella *et al.* (1982). In Fig. 1a the experimental reversals of Hochella *et al.* are shown to be consistent with the calculated slope of reaction 1c; however, the reversals of Olesch require a negative slope that does not match calculations for reactions 1a, 1b, or 1c. Calculations with *Vs(a)* (not shown) do not fit either set of experiments. In Fig. 1b, the reversals of Olesch and of Hochella *et al.* for reaction 2 are consistent with all calculated slopes.

Different starting compositions for Mg-vesuvianite were used by different experimenters, and the actual vesuvianite grown may not correspond to the starting composition because of persistence of additional phases (Hochella *et al.*, 1982). The experiments are also difficult to interpret or compare because of variable and/or uncertain compositions of melilite (although the akermanite component will be fixed at equilibrium for a given P-T by coexistence with monticellite + wollastonite), and because Mg-vesuvianite may break down by a continuous reaction (Hochella *et al.*, 1982). Lacking unambiguous compositional data, we have not attempted to evaluate the experiments on the quartz-absent reaction.

Olesch (1978) and Hochella *et al.* (1982) have obtained experimental data on two quartz-saturated Mg-vesuvianite reactions:



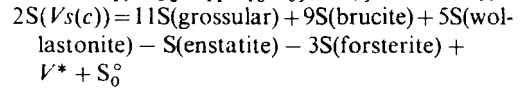
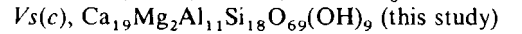
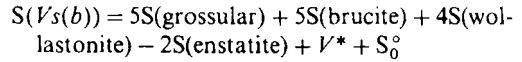
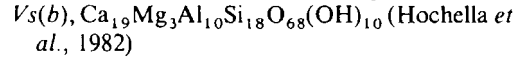
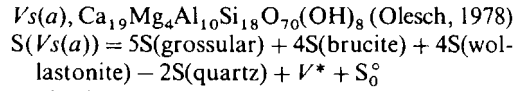
As noted by Hochella *et al.*, reaction 2 is metastable relative to reaction 1 because anorthite + wollastonite will react to form grossular + quartz:



However, the metastability of reaction 2 need not preclude its use in generating other phase equilibria. Olesch (1978) used the starting composition $\text{Ca}_{19}\text{Mg}_4\text{Al}_{10}\text{Si}_{18}\text{O}_{70}(\text{OH})_8$ while Hochella *et al.* (1982) used $\text{Ca}_{19}\text{Mg}_3\text{Al}_{10}\text{Si}_{18}\text{O}_{68}(\text{OH})_{10}$ for the quartz-saturated experiments. Hochella *et al.* erroneously report another Mg-vesuvianite composition in the text of their paper (M. F. Hochella, written communication, 1984). Hochella *et al.* obtained reversals on reactions 1 and 2 which constrain their location to $\sim 100^\circ\text{C}$ lower than the placements of Olesch and with a different slope for reaction 1 (Fig. 1). In the calculations which follow, we will test the internal consistency of experiments by slope calculations for different formulae of Mg-vesuvianite.

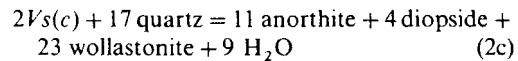
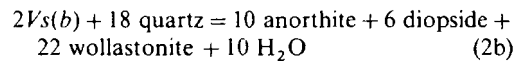
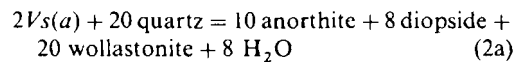
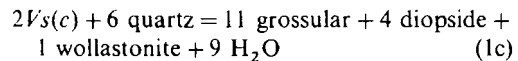
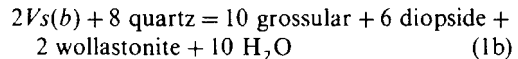
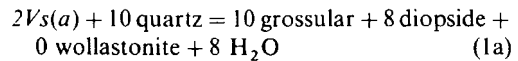
CALCULATION OF VESUVIANITE EQUILIBRIA

There are no published data on the heat capacity or entropy of Mg-vesuvianite, so entropies for three compositions have been estimated by summation techniques similar to those of Fyfe & Verhoogen (1958) and of Helgeson, Delaney, Nesbitt & Bird (1978):



These entropy estimates include a volume correction $V^* = -0.6V/\text{cal}/\text{mol}^\circ\text{C}$ and a zero point entropy $S_0^\circ = -8R[x \ln x + (1-x) \ln(1-x)]$ where $x = 3/8$ for $V_s(a)$, $2/8$ for $V_s(b)$, and $1/8$ for $V_s(c)$. Calculations at $T > 900^\circ\text{K}$ would require extrapolation of S_f for brucite well beyond its measured range and may lead to unacceptably large errors in the estimated entropies.

We have calculated reactions 1 and 2 for each vesuvianite composition from the experimental reversals of Olesch (1978) and Hochella *et al.* (1982). The stoichiometry of each reaction changes depending on which vesuvianite composition is used:



In the case of reaction 1a a compositional degeneracy causes wollastonite to drop out as a product.

The P-T slopes that are calculated for reactions 1c and 2c are similar to those of 1b and 2b and are shown in Fig. 1 for comparison with the experimental results. The slopes calculated for reactions 1a and 2a (not shown) are distinct from those of 1b and 1c or 2b and 2c as a result of the different reaction stoichiometries which are imposed by the different vesuvianite formulae used in our calculations. A negative P-T slope is calculated for reaction 1a at high pressure resulting from the large negative V (reaction) for the solid phases. This calculated curve for 1a is inconsistent with all reversals, while that for 1b and 1c

Table 6. Volumes and entropies used in phase equilibrium calculations

	V ₂₉₈	Ref.*	S ₂₉₈ ^o	Ref.	A†	B†	C†	D†	Ref.
Anorthite	100.79	(1)	47.63	(1)	64.53	13.64	8.33	-381.06	(1)
Brucite	24.63	(1)	15.10	(1)	25.85	1.86	3.69	-152.02	(1)
Diopside	66.09	(1)	34.11	(2)	56.56	5.51	12.95	-335.71	(2)
Forsterite	43.79	(1)	22.49	(3)	37.18	5.57	5.30	-219.40	(1)
Grossular	125.29	(4)	60.87	(5)	107.03	13.79	15.13	-630.95	(1)
Quartz	22.69	(1)	9.909	(1)	17.56	0.19	3.67	-104.24	(1)
Wollastonite	39.93	(1)	19.37	(6)	27.91	2.60	4.36	-164.30	(6)
Enstatite	31.44	(1)	15.84	(6)	25.81	3.66	3.99	-152.61	(6)
V _{5(a)}	867	(7)	445	(9)	732.6	86.6	104.2	-4316.8	(9)
V _{5(b)}	859	(8)	437	(9)	724.4	81.3	103.6	-4266.8	(9)
V _{5(c)}	852	(9)	432	(9)	731.9	84.2	104.8	-4312.3	(9)
	cc/mol		cal/mol ^o K						

* (1) Robie, Hemingway & Fisher (1979); (2) Krupka, Kerrick & Robie (1980); (3) Robie, Hemingway & Takei (1982); (4) Meagher (1980); (5) Westrum, Essene & Perkins (1979); (6) Krupka *et al.* (1980); Hemingway, Haas & Robinson (1982); (7) Olesch (1978); (8) Hochella *et al.* (1982); (9) this paper with V₂₉₈ corrected by -2.7 cc/mol for Fe³⁺ solid solution; S₂₉₈^o estimated (see text).

† $S_T^o - S_{298}^o = A \cdot \ln T + B \cdot 10^{-3} \cdot T + C \cdot 10^5 T^{-2} + D(\text{cal/mol} \cdot ^\circ\text{K})$.

is consistent with the experimental reversals of Hochella *et al.* (1982) but not of Olesch (1978) (Fig. 1). It seems unlikely that the experiments of Olesch are accurately represented by reaction 1a, which implies that his product vesuvianite was not the same composition as his starting reagents. The slope calculations for 1b *vs* 1c and 2b *vs* 2c yield results consistent with the experimental reversals reported by Hochella *et al.* (1982).

Before experiments on Mg-vesuvianite can be accurately extrapolated to higher pressures and temperatures and applied to natural systems, much additional information is needed: (1) the composition of the reactant and product vesuvianite; (2) tight experimental reversals over a much larger P-T range; (3) heat capacity measurements on an end-member Mg-vesuvianite; and (4) complete evaluation of short- and long-range order in synthetic and natural Mg-vesuvianite. Without more complete thermodynamic and compositional information the location of reaction 1 cannot be extended to higher pressures regardless of whose experiments or compositions are preferred.

Potential solid-solutions in synthetic Mg-vesuvianite involving Ca = Mg, MgSi = AlAl and MgOH = AlO are buffered on the univariant reactions by coexistence of the product and reactant phases. If Mg-vesuvianite has significant solid solutions, its composition may vary along the univariant curve and/or the actual reaction may become continuous over a finite temperature range.

T-X EQUILIBRIA AND PETROLOGICAL APPLICATIONS

Vesuvianite is increasingly recognized as an important mineral in metamorphic and metasomatic mineral assemblages. Topological analysis indicates that vesuvianite-bearing equilibria will limit the P-T-X(CO₂-H₂O) conditions for formation of many calc-silicate assemblages. With our new information on the formula of Mg-vesuvianite, more accurate stoichiometries may be calculated for vesuvianite reactions. These are presumably more realistic than those previously proposed because of the improved Mg-vesuvianite formula used to model the reactions and the reasonable agreement of the calculated P-T location of reaction 1c with the reversals of Hochella *et al.* (1982). The modifications of reaction stoichiometry are significant, because the T-XCO₂ slopes of several critical equilibria which define the stability of Mg-vesuvianite change from positive to negative with our vesuvianite formula. It is now possible to comment more realistically on the

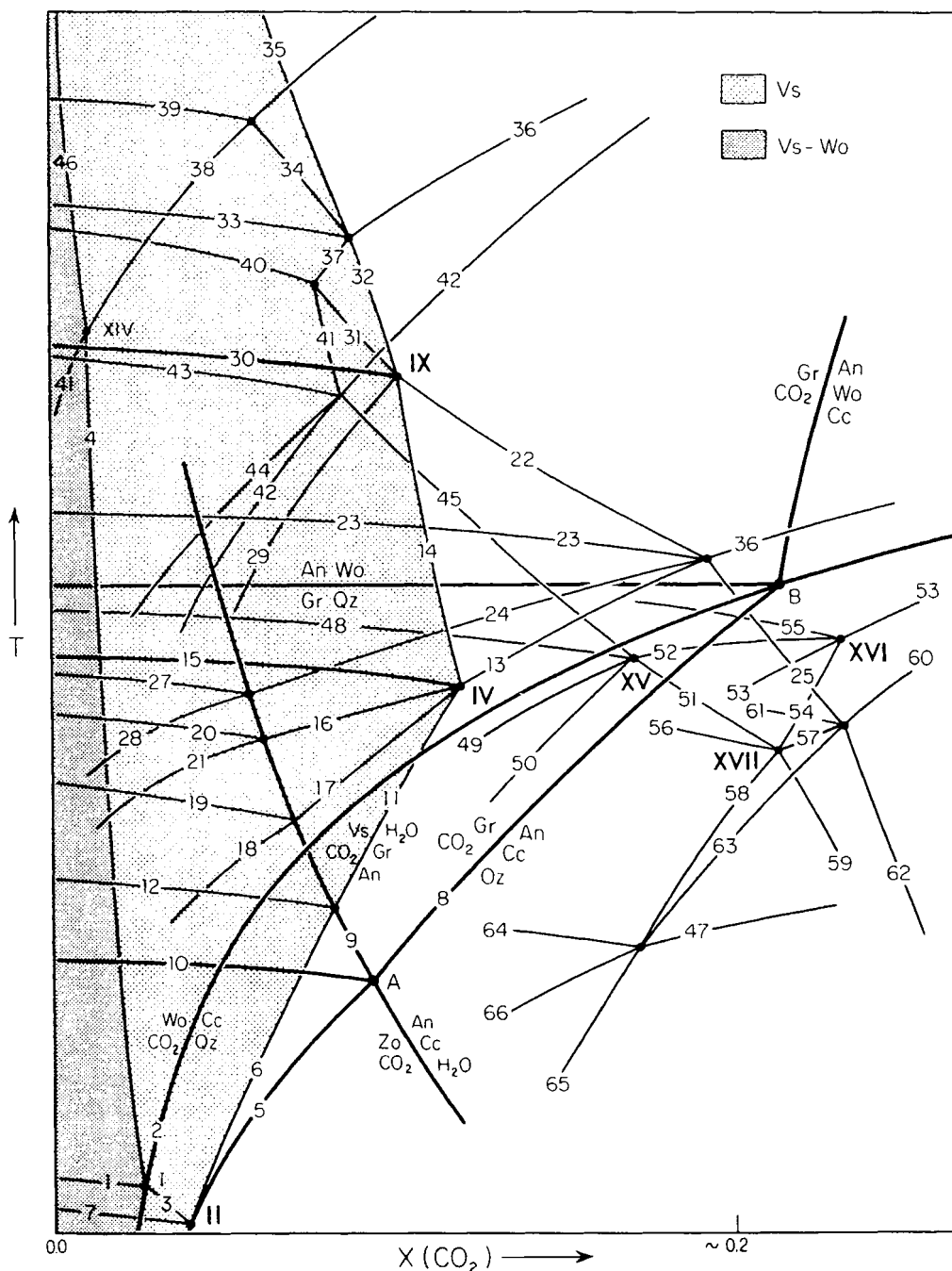
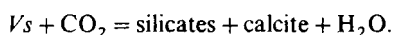


Fig. 2. Schematic T vs $X(\text{H}_2\text{O}-\text{CO}_2)$ plots of equilibria in the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CO}_2-\text{H}_2\text{O}$ at constant P . The assemblages containing Mg - Vs (light stipple) or Mg - Vs + Wo (dark stipple) are restricted to H_2O -rich, CO_2 -poor conditions. Invariant point B has been experimentally located at $X\text{CO}_2 = 0.2$ kbar and thus all Mg -vesuvianite assemblages indicate $X\text{CO}_2 < 0.2$ at this pressure. Reactions and abbreviations are given in Table 7.

significance of naturally occurring vesuvianite-bearing mineral assemblages.

A schematic petrogenetic grid has been constructed for the system CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂ by Schreinemaker's analysis of model reactions involving the phases Mg-vesuvianite (*Vs*), grossular (*Gr*), diopside (*Di*), anorthite (*An*), wollastonite (*Wo*), clinozoisite (*Zo*), clintonite (*Cl*), clinocllore (*Chl*), tremolite (*Tr*), forsterite (*Fo*), monticellite (*Mo*), akermanite (*Ak*), quartz (*Qz*), spinel (*Sp*), calcite (*Cc*), and a CO₂-H₂O fluid. The topology is presented schematically in terms of an isobaric T-XCO₂ diagram (Fig. 2) and four isothermal-isobaric log fH₂O-log fCO₂ diagrams (Fig. 3a-d). Reaction numbers and their stoichiometries for the stable equilibria are listed in Table 7. The composition of Mg-vesuvianite used for calculating reactions involving vesuvianite is that determined in this study—*Vs(c)*. The composition for clintonite is the model stoichiometry used by Rice (1979), CaMg₂Al₄SiO₁₀(OH)₂. The composition of the melilite is assumed to be adequately represented by the formula for akermanite, Ca₂MgSi₂O₇. The topology of invariant points XV, XVI, and XVII in Fig. 3a is equivalent to that of Rice (1979). Further justification of our choice of this topology *vs* others (see, for example, Rice, 1983) is given in Appendix I.

Figures 2 and 3a-d illustrate that the stability of Mg-vesuvianite is limited to the high XH₂O/low XCO₂ side of a series of equilibria (reactions 6, 11, 14, 32, 35) of the type:



These equilibria and the invariant points connecting them (II, III, IV, IX, X) require H₂O-rich fluids within the known stability of grossular (e.g., XCO₂ values less than about 0.2 at P = 1-4 kbar and T < 600°C).

A series of fifteen dehydration equilibria are generated (Table 7) which potentially provide T-XH₂O limits to common calc-silicate assemblages. As examples, reaction 7 provides a maximum fH₂O or minimum T limit for *Gr + Di* assemblages (Figs 2, 3a, 3c) while reactions 12 and 19 define lower fH₂O or upper T limits of stability for the assemblages, *Gr + Di + Zo* and *Di + Zo*, respectively (Figs 2, 3a, 3d).

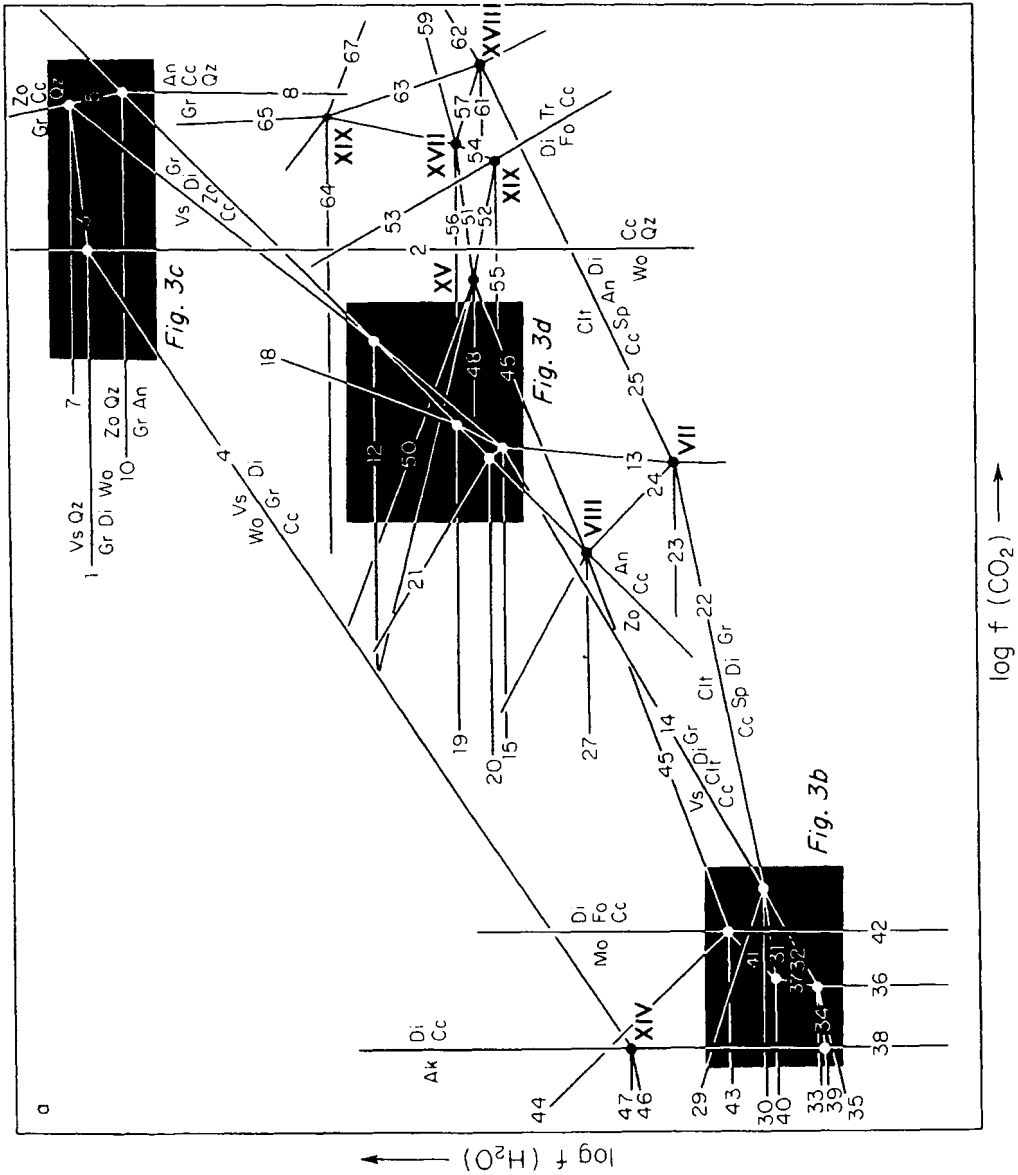
Figure 2 illustrates this topology in terms of an isobaric T-XCO₂ section. Although no T-XCO₂ values are shown, equilibria that have been experimentally calibrated are accurately placed with respect to one another. The T-XCO₂ location of reaction 1 (Fig. 2) is based on the experimentally reversed data of Hochella *et al.*

(1982). The locations of invariant points I, II, and III are realistic if the composition of vesuvianite in the experiments of Hochella *et al.* approximates *Vs(c)*.

It is apparent from the locations of invariant points I and II that the stability of *Vs + Qz* is narrowly restricted to low T and low XCO₂ conditions (approximately T ≤ 400°C and XCO₂ < 0.06 at P_t ≤ 2 kbar) by reactions 1 and 3 (Fig. 2). The reported occurrences of *Vs + Qz* in amphibolite facies metabasites (Braitsch & Chatterjee, 1963; Trommsdorff, 1968) and in hornblende-hornfels facies calc-silicates (e.g. Kerrick *et al.*, 1973; Bowman, 1978) at T > 400°C suggests that solid solutions (involving principally F⁻¹, Fe⁺³ and Ti⁺⁴) in vesuvianite may extend the thermal stability of *Vs + Qz*. The reported occurrences of *Vs + Qz + Wo + Di + Cc* with *Gr*-rich garnet and albitic plagioclase in calc-silicate rocks of Sierra Nevada roof pendants (Kerrick *et al.*, 1973) indicate that albite solid solution in plagioclase (*Pg*) is also involved in modifying the end-member topology (largely by shifts in reactions 8, 9, 11, and 12) to stabilized *Wo + Pg* with *Vs + Qz*.

In contrast to the restricted stability of *Vs + Qz*, the thermal stability of *Vs* in the absence of *Qz* is more extensive, but vesuvianite is still restricted to the low XCO₂ side of the limiting equilibria (reactions 6, 11, 14, 32, 35) (Figs 2, 3a-d). These equilibria must exist in H₂O-rich fluids (XCO₂ < 0.2), because grossular occurs in all the vesuvianite-limiting reactions, and because the vesuvianite-limiting reactions above invariant point IV (reactions 14, 32, 35) have negative T-XCO₂ slopes (Fig. 2). Thus the *maximum* XCO₂ value for the stability of vesuvianite is represented by invariant point IV. The negative T-XCO₂ slopes are the direct result of the stoichiometry of these reactions. Using the previously accepted formula for Mg-vesuvianite, reaction 14 would have a positive T-XCO₂ slope and invariant point IX would be located at higher XCO₂ values. Consequently, our formula for Mg-vesuvianite creates a more restricted stability field for Mg-vesuvianite increasing its petrologic utility as an indicator of water-rich conditions.

It is not presently possible to accurately locate point IV or the *Vs*-limiting equilibria at higher T. However, it is possible to infer reasonable T-XCO₂ slopes of the lower temperature equilibria from consideration of reaction stoichiometry and natural occurrences and to approximately locate point IV. Reactions 6 and 11 have relatively steep, positive T-XCO₂ slopes because of the nearly equal moles of CO₂ and H₂O in the reaction. Topological considerations require invariant point



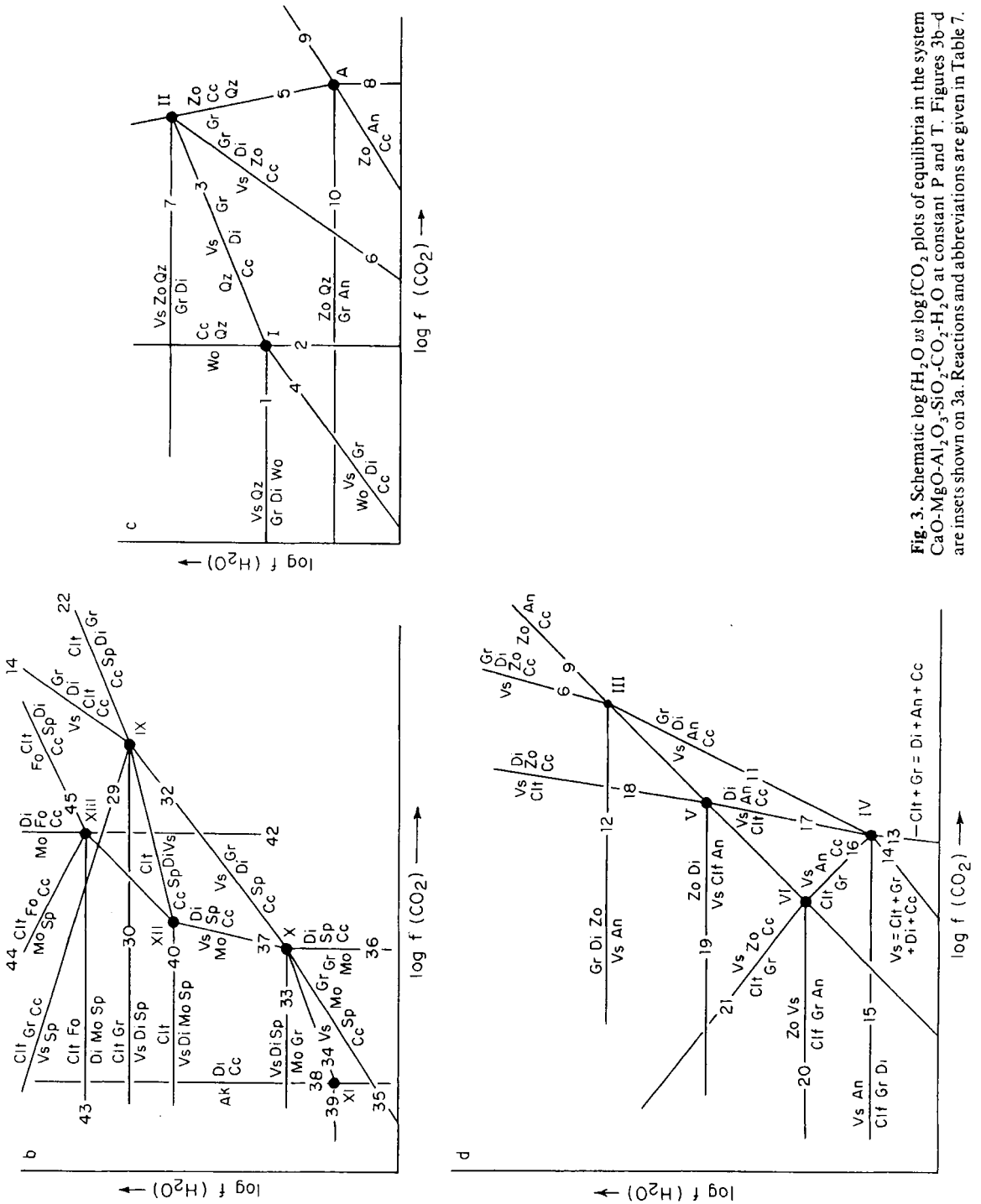


Fig. 3. Schematic $\log f\text{H}_2\text{O}$ vs $\log f\text{CO}_2$ plots of equilibria in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ at constant P and T. Figures 3b-d are insets shown on 3a. Reactions and abbreviations are given in Table 7.

Table 7. List of model equilibria and abbreviations

<i>An</i>	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
<i>Ak</i>	Akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$
<i>Cc</i>	Calcite	CaCO_3
<i>Chl</i>	Clinocllore	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$
<i>Clt</i>	Clintonite	$\text{CaMg}_2\text{Al}_4\text{SiO}_{10}(\text{OH})_2$
<i>Di</i>	Diopside	$\text{CaMgSi}_2\text{O}_6$
<i>Fo</i>	Forsterite	Mg_2SiO_4
<i>Gr</i>	Grossular	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
<i>Mo</i>	Monticellite	CaMgSiO_4
<i>Qz</i>	Quartz	SiO_2
<i>Sp</i>	Spinel	MgAl_2O_4
<i>Vs</i>	Mg-vesuvianite	$\text{Ca}_{16}\text{Mg}_2\text{Al}_{11}\text{Si}_{18}\text{O}_{69}(\text{OH})_9$
<i>Wo</i>	Wollastonite	CaSiO_3
<i>Zo</i>	Clinozoisite	$\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$
(1)	$2Vs + 6Qz = 11Gr + 4Di + Wo + 9H_2O$	
(2)	$Cc + Qz = Wo + CO_2$	
(3)	$2Vs + 5Qz + CO_2 = 11Gr + 4Di + Cc + 9H_2O$	
(4)	$2Vs + 5Wo + 6CO_2 = 11Gr + 4Di + 6Cc + 9H_2O$	
(5)	$2Zo + 5Cc + 3Qz = 3Gr + H_2O + 5CO_2$	
(6)	$3Vs + 14CO_2 = 9Gr + 6Di + 5Zo + 14Cc + 11H_2O$	
(7)	$5Vs + Zo + 4Qz = 29Gr + 10Di + 23H_2O$	
(8)	$An + 2Cc + Qz = Gr + 2CO_2$	
(9)	$2Zo + CO_2 = 3An + Cc + H_2O$	
(10)	$4Zo + Qz = Gr + 5An + 2H_2O$	
(11)	$2Vs + 11CO_2 = 6Gr + 4Di + 5An + 11Cc + 9H_2O$	
(12)	$9Gr + 6Di + 33Zo = 3Vs + 42An + 3H_2O$	
(13)	$Cl + 7Gr + 11CO_2 = 2Di + 9An + 11Cc + H_2O$	
(14)	$18Vs + 44CO_2 = 5Cl + 89Gr + 26Di + 44Cc + 76H_2O$	
(15)	$2Vs + 4An = Cl + 13Gr + 2Di + 8H_2O$	
(16)	$Vs + An + Cc = Cl + Gr + CO_2 + H_2O$	
(17)	$Vs + Cl + CO_2 = Di + An + Cc + H_2O$	
(18)	$21Vs + 9Cl + 170CO_2 = 60Di + 139Zo + 170Cc + 59H_2O$	
(19)	$140Zo + 20Di = 7Vs + 3Cl + 170An + 37H_2O$	
(20)	$11Zo + Vs = Cl + 10Gr + 10An + 9H_2O$	
(21)	$13Zo + 3Vs + 10Cc = 3Cl + 30Gr + 10CO_2 + 17H_2O$	
(22)	$5Cl + CO_2 = Gr + Di + 9Sp + Cc + 5H_2O$	
(23)	$6Cl + An = 2Gr + Di + 11Sp + 6H_2O$	
(24)	$Cl + An + Cc = Gr + 2Sp + CO_2 + H_2O$	
(25)	$4Cl + 2CO_2 = Di + An + 7Sp + 2Cc + 4H_2O$	
(26)	$4Gr + Sp + 6CO_2 = Di + 5An + 6Cc$	
(27)	$Cl + 2Zo = 2An + Gr + 2Sp + 2H_2O$	
(28)	$3Cl + 2Zo + 2Cc = 3Gr + 6Sp + 2CO_2 + 4H_2O$	
(29)	$2Vs + 26Sp + 6H_2O + 2CO_2 = 15Cl + 7Gr + 2Cc$	
(30)	$25Cl + 5Gr = 2Vs + 2Di + 44Sp + 16H_2O$	
(31)	$50Cl + 5CO_2 = 2Vs + 7Di + 89Sp + 5Cc + 41H_2O$	
(32)	$2Vs + 5CO_2 = 10Gr + 3Di + Sp + 5Cc + 9H_2O$	
(33)	$8Vs + 8Di + Sp = 25Mo + 45Gr + 36H_2O$	
(34)	$2Vs + Di + CO_2 = 11Gr + 5Mo + Cc + 9H_2O$	
(35)	$8Vs + 8CO_2 = 15Mo + 43Gr + Sp + 8Cc + 36H_2O$	
(36)	$4Di + Sp + 4Cc = 5Mo + Gr + 4CO_2$	
(37)	$2Vs + 50Mo + 45CO_2 = 43Di + 11Sp + 45Cc + 9H_2O$	
(38)	$Di + Cc = Ak + CO_2$	
(39)	$2Vs + 2Di = 11Gr + 5Mo + Ak + 9H_2O$	
(40)	$45Cl = 2Vs + 2Di + 5Mo + 79Sp + 36H_2O$	
(41)	$Cl + Mo + CO_2 = Di + 2Sp + Cc + H_2O$	
(42)	$Di + Fo + 2Cc = 3Mo + 2CO_2$	
(43)	$2Cl + Fo = Di + Mo + 4Sp + 2H_2O$	
(44)	$Cl + Fo + Cc = 2Mo + 2Sp + CO_2 + H_2O$	
(45)	$3Cl + Fo + CO_2 = 2Di + 6Sp + Cc + 3H_2O$	
(46)	$2Vs + 5Wo + 2CO_2 = 4Ak + 11Gr + 2Cc + 9H_2O$	
(47)	$2Vs + 5Wo + 2Di = 6Ak + 11Gr + 9H_2O$	

Table 7—continued

(48)	$Chl + 2Clt = 2Di + Fo + 5Sp + 6H_2O$
(49)	$6Chl + 5Cc = 3Clt + 2Di + 11Fo + 21H_2O + 5CO_2$
(50)	$Chl + Cc + Sp = Clt + 2Fo + 3H_2O + CO_2$
(51)	$5Clt + Chl + CO_2 = 4Di + 11Sp + Cc + 9H_2O$
(52)	$3Chl + 2Cc = 5Fo + 2Di + 3Sp + 2CO_2 + 12H_2O$
(53)	$3Tr + 5Cc = 11Di + 2Fo + 5CO_2 + 3H_2O$
(54)	$2Chl + 17Di + 7CO_2 = 5Tr + 2Sp + 7Cc + 3H_2O$
(55)	$5Chl + 4Di = 2Tr + 7Fo + 5Sp + 18H_2O$
(56)	$7Clt + Tr + Chl = 9Di + 15Sp + 12H_2O$
(57)	$2Clt + Tr + Cc = 5Di + 4Sp + 3H_2O + CO_2$
(58)	$4Chl + 39Di + 15CO_2 = 2Clt + 11Tr + 15Cc + 3H_2O$
(59)	$17Clt + 5Chl + 9CO_2 = 4Tr + 39Sp + 9Cc + 33H_2O$
(60)	$2Tr + An + 4Cc = 9Di + Sp + 4CO_2 + 2H_2O$
(61)	$8Clt + 2Tr = 11Di + An + 15Sp + 10H_2O$
(62)	$18Clt + 11CO_2 = Tr + 11Cc + 31Sp + 5An + 17H_2O$
(63)	$7Tr + 4An + 15Cc = 2Clt + 31Di + 15CO_2 + 5H_2O$
(64)	$Clt + Tr + 2H_2O = Chl + An + 2Di$
(65)	$9Tr + 2An + 15Cc = 2Chl + 35Di + 15CO_2 + H_2O$
(66)	$7Chl + 11An + 15Cc = 9Clt + 17Di + 15CO_2 + 19H_2O$
(67)	$31Chl + 39An + 30Cc = 17Tr + 35Clt + 30CO_2 + 72H_2O$

III to occur at lower T and lower XCO₂ values relative to invariant point A (Figs 2, 3d). These considerations place point III at XCO₂ ≤ 0.05. The principal uncertainty is the XCO₂ value of invariant point IV and the location of reaction 13. The associations of *Clt* + *Gr*-rich garnet and *Clt* + *Gn* + *Px* + *Sp* + *Cc* (note reactions 22) in magnesian skarns at Elkhorn, Montana, and other areas of the Boulder Batholith which formed at T < 600°C and XCO₂ < 0.3 (Knopf, 1953; Bowman, 1978; Shedlock & Essene, 1979) suggest that reaction 13 and invariant point IV are located at XCO₂ ≤ 0.2.

The upper XCO₂ limit for *Vs* + *Wo* assemblages is restricted, as reactions 4 and 46 both have negative T-XCO₂ slopes (Figs 2, 3a, 3c). Based on the data of Hochella *et al.* (1982), *Vs* + *Wo* assemblages would be restricted to very low values of XCO₂, < 0.03 (Fig. 2).

Compositional data on naturally occurring vesuvianite assemblages and experimental determinations of critical limiting equilibria are needed to rigorously evaluate the stability of vesuvianite as a function of P-T-XCO₂ and to confirm or modify our proposed topology. Given the experimental data of Hochella *et al.* (1982) and reasonable constraints on T-XCO₂ slopes, the topology associated with invariant points I-III and XIV is qualitative, but realistic. Despite these uncertainties, it is clear that Mg-vesuvianite has a wide range of thermal stability but is restricted to H₂O-rich fluids.

It is important to accurately establish the T-XCO₂ stability field for vesuvianite-bearing

assemblages because Mg-vesuvianite potentially provides well-defined restrictions on fluid composition. The accurate location of invariant point IV will provide an accurate determination of the upper XCO₂ limits for the stability of Mg-vesuvianite bearing assemblages. In general, the Mg-vesuvianite reactions define closer T-XCO₂ limits for calc-silicate assemblages than are presently available from other equilibria in the system CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂.

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APPENDIX I

Rationale for Figs 2 and 3

The topology shown in Figs 2 and 3 is constructed through Schreinemaker's analysis starting with a

few well-known, experimentally determined reactions. However, without more detailed thermochemical and experimental data many reactions cannot be quantitatively located and the possibility that some reactions or invariant points may be metastable cannot be discounted.

The primary reason for differences between this topology and others proposed (for example, see Rice, 1983) is our formula for Mg-vesuvianite which changes the slopes of some reactions. We have constructed this topology so as to conform as closely as possible to the stability of natural mineral assemblages, and some of these decisions need further explanation.

The stable existence of invariant points I–III is supported by (1) the experimentally known locations of equilibria involving *Gr*, *Qz*, *An*, *Wo*, *Zo*, and *Cc* (reactions 2, 5, 8, 9, 10) relative to the experimental results of Hochella *et al.* (1982) for the stability of *Vs* + *Qz* (reaction 1); (2) consideration of reasonable T-XCO₂ slopes for reactions 9, 11, 13, and 14, given the required location of invariant point I at T ~ 400°C at P < 2 kbar (Hochella *et al.*, 1982); and (3) consistency of this portion of the topology with reported parageneses of Trommsdorff (1968) and Kerrick *et al.* (1973). Both IV and VII are thought to be stable invariant points, based on the occurrences of *Vs* + *Gn* + *Px* + *Cc* and *Cl* + *Gn* + *Px* + *Sp* + *Cc* (rare) in contact magnesian skarns (Knopf, 1953; Shedlock & Essene, 1979; Bowman & Essene, 1984). These are associated with skarns forming at T < 600°C and P < 2 kbar (Shedlock & Essene, 1979; Bowman & Essene, 1984), so we infer invariant points IV and VII occur at temperatures below the breakdown of grossular-quartz. Rice (1979) has presented several arguments for the stable existence of invariant points XV–XVII, including natural occurrences of clintonite-bearing assemblages consistent with this topology.

The topology of the equilibria is unclear at lower total X(H₂O-CO₂) values, although Fig. 2 is consistent with naturally occurring vesuvianite-bearing assemblages. An alternative topology is generated if reactions 45 and 22 intersect, instead of 45 and 42, which results in a set of limiting equilibria which contain grossular and forsterite as breakdown products of vesuvianite. As we are unaware of *Vs* + *Gr* + *Fo* or *Cl* + *Gn* + *Fo* assemblages, we prefer Fig. 2. It is important to note that in either alternative a series of reactions (14, 32, and 35 or other equivalent) is generated which limits the stability of *Vs* to high ratios of H₂O/CO₂. Figures 2 and 3a predict the stability of such high-temperature assemblages

as *Vs* + *Mo* + *Gr* + *Px* + *Cc* (reaction 34), *Vs* + *Mo* + *Px* + *Sp* + *Cc* (reaction 37), and *Vs* + *Px* + *Mo* + *Gr* + *Sp* (reaction 33), all of which have been reported from the granulite facies calc-silicates in the Cascade Slide area of the Adirondacks, New York, USA (Tracy *et al.*, 1978; Valley & Essene, 1979). This topology is also consistent with occurrences of *Vs* + *Cl* + *Mo* + *Sp* + *Cc* in the Clark Mountain Thrust area, California, USA (Adams & Anderson, 1979).

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