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Coexisting rhodonite and pyroxmangite in the system $MnSiO_3$-$CaSiO_3$-$MgSiO_3$-$FeSiO_3$ as a geothermometer*

by *R. Schultz-Güttler*[1], *Tj. Peters*[2]

Abstract

Using the systematic trends in the crystal chemistry of the pyroxenoid series and the stabilities of rhodonite and pyroxmangite with pure $MnSiO_3$ composition, an empirical equation was developed which permits the estimation of the equilibrium temperature of coexisting pyroxenoids. Application to natural occurrences showed in general agreement between independent estimated conditions and calculated temperatures. The proposed equation can be used as a geothermo-barometer. Calculated temperatures of most occurrences coincide with the estimated peak conditions of metamorphism. Intimate intergrowths and exsolutions tend to decrease the estimated temperature.

Keywords: Rhodonite, pyroxmangite, geothermometry, geobarometry.

Introduction

The coexistence of the pyroxenoids rhodonite and pyroxmangite in metamorphosed manganese-bearing rocks has, among others, been described by CHOPIN (1978), PETERS et al. (1977, 1978), SCHULTZ-GÜTTLER (1986) and WINTER et al. (1981). Although the phase relations for the pure $MnSiO_3$ composition are reasonably well known (MARESCH and MOTTANA, 1976; AKIMOTO and SYONO, 1972), these results could, up to now, not be used to determine the P–T conditions of natural compositions (WINTER et al., 1981).

This may be partly explained by the small values of the enthalpies and entropies of transition (SCHULTZ-GÜTTLER, 1986). The other reason leading to problems in the derivation of a geothermometer and/or geobarometer is linked with the great extent and variety of cationic substitutions possible in these phases, pyroxmangite with seven cation sites and rhodonite with five. The various possibilities of cation distributions among them makes the application of any mixing model very difficult. The site populations should be known for each phase, the interaction parameter, the enthalpies and entropies of transitions for unstable and members, their P and T dependence, and so on. Even more problems are apparent due to possible disordered intergrowths of structural units in the pyroxenoid serie as shown by high resolution electron microscopy (HRTEM) (CZANK and SIMONS, 1983; RIED et al., 1980; JEFFERSON et al., 1980; CATLOW et al., 1982).

ANGEL et al. (1984) explain the phase transitions in this series of structures with the action of shear along crystallographic planes. CZANK and SIMONS (1982) show the chemical control on the amount of type and frequency of chain periodicity faults in pyroxenoids. CZANK and LIEBAU (1980) discuss the behaviour of this class of structures as a continuous series in P–T–X space. These evidences of gradual

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* Dedicated to Professor Ernst Niggli on the occasion of his 70th birthday.

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transformation due to increase in structural disorder by changes in P, T or chemical composition facilitate the approximate treatment shown below to develop a geothermometer-barometer for these phases.

Volume relations of pyroxmangite and rhodonite

The strong correlation between enthalpies of formation from the oxides and periodicity (Liebau, 1985) of the chains and, likewise, between P and volume discussed by Schultz-Güttler (1986) makes it likely that the energetic relations between coexisting phases of pyroxenoids are mainly a function of the bulk volumes. Under the assumption of preponderance of the true periodicities (5 = rhodonite, 7 = pyroxmangite) the molvolumina of both have been determined from experimental data as a function of substitution by Ca, Mg and Fe (Ito, 1972; Harneit, 1981; Simons, 1978; Abrecht and Peters, 1980; Hübner, 1986) and result in equations (1) and (2):

$$(1)\quad V_{\mathrm{rhodonite}} = 34.958 + 1.744X_{\mathrm{CaSiO_3}} - -3.367X_{\mathrm{MgSiO_3}} - 1.711X_{\mathrm{FeSiO_3}}\ (\mathrm{cm^3/mol})$$

$$(2)\quad V_{\mathrm{pyroxmangite}} = 34.6618 + 1.576X_{\mathrm{CaSiO_3}} - 3.113X_{\mathrm{MgSiO_3}} - 1.424X_{\mathrm{FeSiO_3}}\ (\mathrm{cm^3/mol})$$

It is interesting to note that $\partial V/\partial VX_{\mathrm{Ca}}$ in pyroxmangite is smaller than in rhodonite in accordance with a slightly larger mean M(5)–O distance and the possibility of two sites for Ca in the pyroxmangite structure (Narita et al., 1977). On the other hand, the relative change of volume due to Ca substitution, or the relation $d\Delta V_{\mathrm{CaSiO_3}}/V_{\mathrm{pyroxenoid}}$ is 0.049888 for rhodonite and 0.045468 for pyroxmangite, showing the similarities in substitution mechanism. The substitution of Mg in both structures decreases the volumes but again, to a smaller amount in pyroxmangite than in rhodonite, probably reflecting slight differences in bond distances. It should be remembered that all sites in the structures of pyroxmangite or rhodonite of $MnSiO_3$ composition have sizes that allow the easy substitution of Ca in the larger sites (M–O ~ 2.40) and Mg and Fe in the smaller ones (M–O ~ 2.20) (Narita et al., 1977). Besides the use of some synthetic products, more weight has been lent to the X–V relations of natural minerals to minimize the disturbing influence of possible chain periodicity faults on the volumes. It is difficult to estimate the standard deviations of the volumes as an influence of these substitutions, but a check on data cited by Harneit (1981) confirmed the values for Ca and Mg at least in rhodonite. Pyroxmangite has been much less investigated and the values shown in equation (2) may have larger deviations than in the case of rhodonite. Distribution of cations other than Mn on more than one site in the structure may show up as values differing from the ones shown in equations (1) and (2). In that case, they would be smaller. As nearly all bond lengths of sites suitable for multiple substitutions are much larger than the Mg–O or Fe–O bond length in the respective oxides, this problem may be neglected.

Accepting equations (1) and (2) as valid for relatively well ordered (structural as well as cationic) pyroxenoids, it is possible to calculate the volume change of the phase transformations, at least at room temperature.

$$(3)\quad \Delta V^{1\,\mathrm{bar}}_{298,15} = 0.2962 + [(1.744X^{\mathrm{Rhod}}_{\mathrm{CaSiO_3}} - 1.576X^{\mathrm{Pyxm}}_{\mathrm{CaSiO_3}}) - (3.367X^{\mathrm{Rhod}}_{\mathrm{MgSiO_3}} - 3.113X^{\mathrm{Pyxm}}_{\mathrm{MgSiO_3}}) - (1.711X^{\mathrm{Rhod}}_{\mathrm{FeSiO_3}} - 1.424X^{\mathrm{Pyxm}}_{\mathrm{FeSiO_3}})]\ (\mathrm{cm^3/mol})$$

To show the importance of the volume change due to substitutions, one example is calculated: rhodonite with 20 mol% $CaSiO_3$ and pyroxmangite with 10 mol% $CaSiO_3$ have $\Delta V_R = 0.4874\ \mathrm{cm^3/mol}$, which is much larger than ΔV for the $MnSiO_3$ composition ($0.2962\ \mathrm{cm^3/mol}$). From the relation $d\Delta G_R/dP = +\Delta V_R$ at constant temperature, this example immediately shows the strong energetic influence of ΔV_R, especially in cases with small ΔH_R and ΔS_R.

Empirical equation for geothermobarometry and application to natural occurrences

As a first approximation to the true thermodynamic behaviour of the system $MnSiO_3$, the phase relations between rhodonite and pyroxmangite, as shown by MARESCH and MOTTANA (1976), may be used. The experimental data displayed in their work show a phase boundary approximating a straight line over a large P–T interval. It is true that the experimental brackets are not very narrow and quite a range of possible values of dP/dT can be derived from the data. These values cover about 55 to 44 (b/°K). MARESCH and MOTTANA (op. cit.) opt for equation (4) as the most probable describing the equilibrium between rhodonite and pyroxmangite:

(4) $P = -32223 + 49.5\,T$ (°K, bar)

Independent calorimetric work by AKAOGI and NAVROTSKY (1985) at 974 °K and the use of the Clapeyron equation $\frac{\Delta H}{T\Delta V} = \frac{dP}{dT}$ (LEWIS and RANDALL, 1961) permitted the evaluation of the slope dP/dT as 51.40 (b/°K) for all reactions between the members of the pyroxenoids. This slope and an equilibrium pressure of 16.0 kb at 974 °K from MARESCH and MOTTANA'S work (1976) result in:

(5) $P = -34073 + 51.4\,T$ (°K/bar).

Equations (4) and (5) are very similar to the thermodynamic equation of state of the form given by LEWIS and RANDALL (op. cit.) in terms of the internal energy E

(6) $$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T$$

Equation (6) may be formulated as

(7) $$P = T\left(\frac{dP}{dT}\right)_V - \left(\frac{dE}{dV}\right)_T$$

describing the relation between external pressure and temperature T as a function of the difference of an equation of state for each substance.

In equation (7), T (dp/dT) = $\Delta H_R/\Delta V_R$, and equation (7) may be formulated as:

(8) $$P = \frac{\Delta H_R}{\Delta V_R} - \left(\frac{dE_R}{dV_R}\right)_T$$

and the equilibrium pressure P is the difference between the coefficients of enthalpy of reaction and volume of reaction and of the difference in internal energy and volume change.

$\Delta H_R/\Delta V_R$ or $T(\frac{dP}{dT})$ from the data of MARESCH and MOTTANA (1976) results in 48213 bar/mol at 974 °K and 16 kb, a value which can be compared to 50064 bar/mol from calorimetric work and systematic trends in the series of pyroxenoids (SCHULTZ-GÜTTLER, 1986). The difference between both values is small and the agreement satisfactory. The transformation temperature at 1 bar is 663 °K from equation (5) or 651 °K (equation (4)).

Results from PINCKNEY et al. (1981) indicate a transformation temperature near 400 °C (673 °K). From the anomalous behaviour of ∂V/∂T between ca. 350 and 400 °C, $T_{\mathrm{Transformation}}$ is concluded to be between 380–400 °C or 653–673 °K.

The type of phase transformation is considered martensitic by HAZEN and FINGER (1981), by ANGEL et al. (1984) due to shear, and by LIEBAU and CZANK (1980) continuous with increasing chain periodicity faults. This explains why normally applied procedures to describe phase equilibria may fail in this case, as shown by WINTER et al. (1981).

But whatever the mechanism, the difference in free energy or chemical potential between both phases must approach zero at equilibrium. It is supposed in the following, that the relative volume changes due to changing P, T, X play the dominant role in the transformation. This treatment parallels the one discussed by VAN HECKE (1985), with these assumptions:

(9) $$\Delta\bar{G} = 0 = 354.628 - 0.534956\,T - d\Delta V(X)P$$

transformed to determine $T_{\Delta\bar{G} = 0}$

(10) $$T = 354.628 - d\Delta V(X)P\,/\,0.534956$$

$d\Delta V(X)$ is the change in volume due to the different substitution of Ca, Mg and Fe, 354.628 (cal/mol) the $\Delta H_{\mathrm{Transit}}$ at 1 bar, 0.534956 (cal/mol°K) ΔS_R at 1 bar and $T_{\mathrm{Transformation}}$ of 662.91 °K. Both values are considered constant. Equation (10) represents a bundle of lines in P-T-X space with different dp/dT slopes pointing to the common transformation temperature of pure $MnSiO_3$, 662.91 °K at 1 bar. The term $d\Delta V(X)$ can be derived from equation (3) and is

$$(11)\ d\triangle V(X) = (0.08047X^{Rhod}_{MgSiO_3} - 0.0744X^{Pyroxm}_{MgSiO_3} - (0.04168X^{Rhod}_{CaSiO_3} - 0.03766X^{Pyroxm}_{CaSiO_3}) + (0.0409X^{Rhod}_{FeSiO_3} - 0.03403X^{Pyroxm}_{FeSiO_3})\ \text{cal/bar}$$

For the few descriptions of coexisting rhodonites and pyroxmangites with chemical data from such divers localities as Brazil, Buritirama (PETERS et al., 1977 and SCHULTZ-GÜTTLER, 1986), the Alps, Alagna and Val Scerscen (PETERS et al., 1978; CHOPIN, 1978) and Bald Knob, North Carolina, U.S.A. (WINTER et al., 1981), the temperatures were estimated using equations (10) and (11).

Reasonable metamorphic temperatures (Table 1) may be calculated for the occurrences of the Alps and of Brazil. In both cases, pyroxmangite and rhodonite are present in subequal amounts and they may be in true equilibrium. Some scatters in temperature are apparent, and this may reflect some heterogenous grains, a problem often encountered by coexisting pyroxenoids (SCHULTZ-GÜTTLER, 1986).

Tab. 1 Calculated temperatures for the coexistence of rhodonite and pyroxmangite from chemical data given in the literature. Shown are the estimated conditions for the localities and the calculated temperatures (equations (10) and (11)).

Alps
CHOPIN (1978):
450 ± 20°C and 6–8 kb
$T_1 = 417$ °C $T_2 = 451$ °C $T_3 = 436$ °C
$T_4 = 438$ °C
$T_5 = 439$ °C (T_1–T_5 refers to different pairs)
all at 7 kb

PETERS et al. (1977):
Alagna: 450 ± 50°C 5 ± 2 kb
$T_1 = 420$ °C 5 kb and 426 °C 6 kb
Val Scerscen: 420 ± 30°C 3 ± 2 kb
$T_1 = 406$ °C 3 kb and 412 °C 4 kb

Brazil
SCHULTZ-GÜTTLER (1986) and PETERS et al. (1978):
Buritirama: 550°C ± 20°C 3 ± 1 kb
$T_1 = 508$ °C 3 kb and 547 °C 4 kb
$T_2 = 514$ °C 3 kb and 556 °C 4 kb
$T_3 = 518$ °C 3 kb and 561 °C 4 kb

U.S.A.
WINTER et al. (1981):
Bald Knob, North Carolina: 575 ± 40°C, 5 ± 1 kb

8 – 9/17	494°C 5 kb	536°C 7 kb
8 – 15/16	474°C 5 kb	510°C 7 kb
18 – 8/ 9	432°C 5 kb	448°C 7 kb
18 – 14/16	437°C 5 kb	454°C 7 kb
18 – 12/14	424°C 5 kb	436°C 7 kb

The temperatures calculated for the Bald Knob (U.S.A.) occurrences (575 °C, 5 kb) seem low for the estimated conditions of this locality. One combination of coexisting pairs, 8–9 and 8–17, however, gives 536 °C, not at 5 kb total pressure as estimated by the authors, but at 7 kb. WINTER et al. (1981) do not give modal abundances and they have (as stated) analysed intergrowths of both phases, resulting in general lower temperatures. On the other hand, the temperatures may reflect a blocking temperature for exsolution. Comparing the calculated temperatures with equilibrium temperatures for the pure $MnSiO_3$ composition, most fall below the latter. One exception is at Buritirama, Brazil, with temperatures about 80 to 100 °C higher than for pure $MnSiO_3$. The high Mg-content of these phases has apparently increased the stabilities, despite the high Ca-content of the rhodonites.

These results seem to confirm that volume is the determining factor for the phase transformation of rhodonite-pyroxmangite. If the phase transformations are controlled by structural instabilities, equations (10) and (11) can be applied for estimation of metamorphic conditions of manganese bearing rocks. On the other hand, it is also possible that the success of these equations is due to cancelling effects of simultaneous substitutions of Ca and Mg on the equilibrium constant K as a function of temperature and composition leaving K essentially unity over the compositional range of these phases.

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References

ABRECHT, J. and PETERS, Tj. (1980): The miscibility gap between rhodonite and bustamite along the join $MnSiO_3$–$Ca_{0.60}Mn_{0.40}SiO_3$. Contr. Mineral. Petrol., 74, 261-269.

AKAOGI, M. and NAVROTSKY, A. (1985): Calorimetric study of high pressure polymorphs of $MnSiO_3$. Phys. Chem. Min., 12, 317-323.

AKIMOTO, S. and SYONO, Y. (1972): High pressure transformations in $MnSiO_3$. Amer. Mineralogist, 57, 76-84.

ANGEL, R.J., PRICE, G.D. and PUTNIS, A. (1984): A mechanism for pyroxene-pyroxenoid and pyroxenoid-pyroxenoid transformations. Phys. Chem. Min., 10, 236-243.

CATLOW, C.R.A., THOMAS, J.M., PARKER, S.C. and JEFFERSON, D.A. (1982): Simulating silicate structures and the structural chemistry of pyroxenoids. Nature, 295, 658-662.

CHOPIN, C. (1978): Les paragenèses réduites ou oxydées de concentrations manganésifères des «schistes lustrés» de Haute-Maurienne (Alpes Françaises). Bull. Soc. Franç. Mineral. Cristallogr., 101, 514-531.

CZANK, M. and LIEBAU, F. (1980): Periodicity faults in chain silicates: a new type of planar lattice faults observed with high resolution electron microscopy. Phys. Chem. Min., 6, 85-93.

CZANK, M. and SIMONS, B. (1982): Superperiodizitäten in $Mn_7(Si,Ge)_7O_{21}$ - elektronenmikroskopische Untersuchung. Z. Kristallogr., 159, 28-30.

CZANK, M. and SIMONS, B. (1983): High resolution electron microscopic studies on ferrosilite III. Phys. Chem. Min., 9, 229-234.

HARNEIT, O. (1981): Kristallographische und chemische Untersuchungen an Mangan-Pyroxenoiden. Unpubl. Diploma thesis, Univ. of Braunschweig, BRD.

HAZEN, R.M. and FINGER, L.W. (1982): Comparative Crystal Chemistry. Wiley, New York.

HÜBNER, J.S. (1986): Nature of phases synthesized along the join $(Mg,Mn)_2Si_2O_6$. Amer. Mineralogist, 71, 111-123.

ITO, J. (1972): Synthesis and crystal chemistry of Li-hydro-pyroxenoids. Mineral. J. Japan, 7, 45-65.

JEFFERSON, D.A. and PUGH, N.J. (1981): The ultrastructure of pyroxenoid chain silicates. III. Intersecting defects in a synthetic iron-manganese pyroxenoid. Acta crystallogr., A37, 281-286.

LIEBAU, F. (1985): Structural Chemistry of Silicates. Springer Verlag Berlin - Heidelberg - New York, 330 p.

LEWIS, G.N. and RANDALL, M. (1961): Thermodynamics. McGraw Hill Book Company New York, Toronto, London, 705 p.

MARESCH, W.V. and MOTTANA, A. (1976): The pyroxmangite-rhodonite transformation for the $MnSiO_3$ composition. Contr. Mineral. Petrol., 55, 69-79.

NARITA, H., KOTO, K. and MORIMOTO, N. (1977): The crystal structures of $MnSiO_3$ polymorphs (rhodonite- and pyroxmangite-type). Mineral. J. 8, 329-342.

PETERS, Tj., SCHWANDER, H., TROMMSDORFF, V. and SOMMERAUER, J. (1978): Manganese pyroxenoids and carbonates: critical phase relations in metamorphic assemblages from the Alps. Contr. Mineral. Petrol., 66, 383-388.

PETERS, Tj., VALARELLI, J.V., COUTINHO, J.M.V., SOMMERAUER, J. and VON RAUMER, J. (1977): The manganese deposits of Buritirama (Parà, Brazil). Schweiz. mineral. petrogr. Mitt., 57, 313-327.

PINCKNEY, L.R., FINGER, L.W., HAZEN, R.M. and BURNHAM, C.W. (1981): Crystal structure of pyroxmangite at high temperature. Ann. Rep. Yb. Carnegie Instn. Washington, 80, 380-384.

RIED, H. and KOREKAWA, M. (1980): Transmission electron microscopy of synthetic and natural Fünferketten and Siebenerketten pyroxenoids. Phys. Chem. Min., 5, 351-365.

SIMONS, B. (1978): Pyroxen-Pyroxenoid-Umwandlungen im System $FeSiO_3$-$MnGeO_3$-$FeGeO_3$ unter hohen Drücken und hohen Temperaturen. Dissertation, Techn. Hochschule Aachen, BRD.

SCHULTZ-GÜTTLER, R. (1986): Constraints on thermodynamic data for the system $MnSiO_3$. Submitted to: Contr. Mineral. Petrol.

VAN HECKE, G.R. (1985): The equal by analyses. A comprehensive thermodynamics treatment for the calculation of liquid crystalline phase diagrams. J. Phys. Chem., 89, 2058-2064.

WINTER, G.A., ESSENE, E.J. and PEACOR, D.R. (1981): Carbonates and pyroxenoids from the manganese deposit near Bald Knob, North Carolina. Amer. Mineralogist, 66, 278-290.

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