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WOLLASTONITE: STABILITY IN H_2O-CO_2 MIXTURES AND OCCURRENCE IN A CONTACT—METAMORPHIC AUREOLE NEAR SALMO, BRITISH COLUMBIA, CANADA

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Abstract

The stability of wollastonite, $CaSiO_3$, has been determined in supercritical mixtures of H_2O and CO_2 at pressures of 1000 bars and 2000 bars. The results are presented and applied to a natural occurrence of the mineral in a contact aureole. An 'isograd' can be drawn between rocks containing calcite+quartz and rocks containing wollastonite+either calcite or quartz. This boundary roughly parallels the intrusive contact, but is closer to the granite near convex contacts and farther from it near concave (embayment) contacts. This general regularity is broken locally by extreme discordance between the boundary and presumed 'maximum temperature' isotherms. The general regularity is consistent with the flow of heat from an irregular intrusion, and the local divergence from broad regularity is consistent with local variations in the proportions of H_2O and CO_2 in the pore fluid.

Introduction

Wollastonite is a common mineral of contact metamorphosed limestones, and not unknown in regional metamorphic rocks. It frequently occurs with hydrous minerals and in environments where one may reasonably assume the presence of some H_2O. It is of interest therefore to know something of the effect of diluting with H_2O the CO_2 produced during its formation. Experimental data on this system was collected and reported upon in a preliminary way at an earlier date (Greenwood, 1962). This report is a brief account of the data and methods used together with an application to a natural occurrence.

Experimental Methods and Theory

The reaction

$$CaCO_3+SiO_2=CaSiO_3+CO_2$$

has been studied by placing unsealed platinum containers holding about fifty milligrams of either $CaSiO_3$ or an equimolar mixture of $CaCO_3+SiO_2$ in a Morey bomb, and introducing CO_2 and H_2O into the bomb. Approximately 1 gm of SiO_2 is placed in the bottom of the bomb to saturate the gas with respect to SiO_2. The bomb is placed in a nichrome-wound resistance furnace and brought to the operating temperature, a process that takes from 90 to 120 minutes, depending on the final temperature. The bomb is maintained at the desired temperature and pressure for a period of from five to more than one hundred days, with constant monitoring of both pressure and temperature, after which time the gas is rapidly extracted and analysed. The bomb is immediately opened and the run products examined by both X-ray and optical methods. Temperature uncertainties for each experiment are shown in Table 1. The analysis of the gas phase is precise to approximately 1 percent. Complete details of the experimental procedures may be found in Greenwood (1961, 1967).

Every experiment reported in Table 1 represents a reversal of the equilibrium, and although many other experiments were performed none contradict the position of the equilibrium as inferred from Table 1. It is also worth reporting that the CH_4 content of the gases in the bombs is less than 0.5% in all cases, and in most it is below the limit of detection (0.01% by volume; gas chromatography). The gas mixtures are thus essentially binary mixtures of H_2O and CO_2 and may be treated as such for theoretical purposes.

TABLE 1. EXPERIMENTAL DATA FOR THE EQUILIBRIUM REACTION
Calcite+quartz+$H_2O \rightleftharpoons$Wollastonite+CO_2+H_2O

Temp., °C	x_{CO_2}	% reacted	Time, days	Run No.
Pressure = 1000 bars, Ca+Q→Wo				
491±1	0.048	50	32	W-4
498±3	0.014	10	26	W-6
647±2	0.196	50	7	W-11
626±2	0.346	30	5	CW-8
625±1	0.429	10	39	CW-11
659±1	0.724	2	21	CW-14
685±3	1.000	25	25	H & T*
685±4	0.891	60	20	CW-16
565±6	0.190	30	31	CW-20
Pressure = 1000 bars, Wo→Ca+Qtz				
476±2	0.392	100	4	CW-5
541±3	0.372	100	3	CW-6
589±2	0.390	50	4	CW-7
609±2	0.378	10	8	VW-9
590±3	0.648	50	20	CW-10
616±3	0.688	20	14	CW-12
639±2	0.685	10	15	CW-13
558±4	0.234	10	24	CW-19
560±3	0.351	25	18	CW-18
662±3	1.000	10	25	H & T*
Pressure = 2000 bars, Ca+Qtz→Wo				
703±3	0.529	70	10	CW-21
679±5	0.514	90	24	CW-23
711±3	0.793	30	10	CW-26
720±3	0.364	100	44	CW-27
723±3	0.891	20	89	CW-31
590±2	0.161	25	72	CW-33
750±3	1.000	25	60	H & T*
Pressure = 2000 bars, Wo→Ca+Qtz				
645±4	0.545	5	8	CW-22
658±2	0.467	10	6	CW-24
701±4	0.821	5	27	CW-25
595±3	0.205	10	34	CW-28
588±5	0.292	100	108	CW-34
725±4	1.000	20	50	H & T*

* Experiments reported by Harker and Tuttle (1956).

Theory relevant to reactions of the kind studied here has been presented by Greenwood (1962, 1967) and need not be repeated here except to indicate the form of the equilibrium boundaries in P-T-x space. It can be shown that the slope of an isobaric T-x boundary is given by

$$\left(\frac{\partial T}{\partial x}\right)_{P,\gamma}^{id} = \frac{RT^2}{\Delta H_r}\cdot\frac{1}{x} \tag{1}$$

where *id* refers to the assumption of ideal mixing in the gas phase, subscripts P,γ refer to constant total pressure and activity coefficients of the gas species, ΔH_r refers to the enthalpy of reaction at the specific constant pressure, and x is the mole fraction of CO_2 in the gas mixture. This expression may be integrated on the assumption that ΔH_r does not change with changing temperature, to give

$$\frac{\Delta H_r}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right] = \ln x_0 - \ln x \tag{2}$$

where T_0 and x_0 are the temperature and mole fraction of CO_2 at the initial point of the integration. This expression gives the isobaric change of equilibrium temperature with change of composition of the coexisting gas phase.

The data of Table 1 are presented graphically in Figure 1, where it may be seen that the general form of boundary required by equation (1) is produced. The brackets on the position of the equilibrium are rather narrow, being not more than about 10°C, and for the most part closer to 5°C. This close control permits an estimate of the ideality of mixing of supercritical mixtures of H_2O and CO_2 over the range of the phase equilibration experiments. The approach adopted for this estimate was to calculate the position of a boundary that would pass through the center of the narrowest experimental bracket, using equation (2) and a value of ΔH_r taken from the experimental curve of Harker and Tuttle (1956) corrected to constant total pressure by means of the expression

$$\Delta \log f = -\frac{\Delta V_s(P - Pex)}{2.303\,RT} \tag{3}$$

(Eugster and Wones, 1962). The value of ΔH_r (2000 bars) that was used was ΔH_r,2kb$=22.9$ kcal mol^{-1}. The result of this calculation produced the solid boundaries shown in Figure 1. It is obvious that the agreement between the experimental points and the assumptions of ideal mixing of CO_2 and H_2O and constant ΔH_r,2kb is execllent. Experimental curves of this kind are not very sensitive to moderate departures from ideal mixing. For example, the 2 kilobar experiments are not contradicted by the

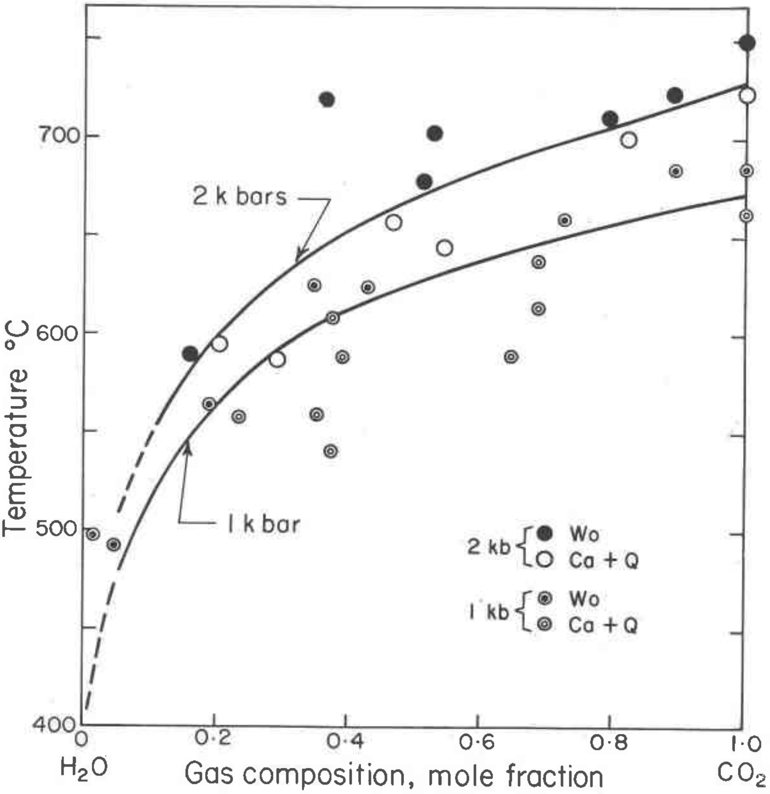

FIG. 1. Stability relations of calcite, quartz, and wollastonite in supercritical mixtures of H_2O and CO_2. Data points taken from Table I. Upper curve, two kilobars, lower curve one kilobar. Total pressure equals fluid pressure, gas compositions in mole fraction of CO_2. Curves calculated assuming ideal mixing of CO_2 and H_2O. Pure CO_2 points from Harker and Tuttle, 1956.

calculated curve until assumed activity coefficients differ from 1.00 by more than about 15 percent, and it is not possible, therefore, to set narrow limits on the degree of ideality of mixing of these gases in this way, even with a narrowly bracketed curve. This fact may be a disadvantage for one who wishes to estimate activity coefficients in this way, but it is a distinct advantage to those who wish to calculate equilibrium boundaries for mineralogical reactions in gas mixtures on the assumption of ideal mixing of gases. It can safely be stated that from the solid-gas phase equilibrium standpoint, CO_2 and H_2O mix ideally in the pressure range below two kilobars in the temperature range above about 500°C. Undoubtedly at lower temperatures and/or higher pressures the situation will be different, and the mixtures will not only be non-ideal, but probably non-binary as well (French, 1966).

A NATURAL OCCURRENCE NEAR SALMO, BRITISH COLUMBIA

The Victory Tungsten property near Salmo, British Columbia, was mapped by the writer at a scale of 1 inch = 100 feet during the summer of 1952, and revisited during the summer of 1962. In 1962 some of the details of the mapping were rechecked and the diamond drill core, which was miraculously still preserved in good condition, was reexamined and sampled, and the original core logs of the writer were rechecked for accuracy. The results of these studies are presented in Figures 2, 3, and 4.

The map area shown in Figure 2 is an area 1500 feet square approximately centered on Lat. 49° 08′ 30″ N; Long. 117° 10′ 41″ W. The area

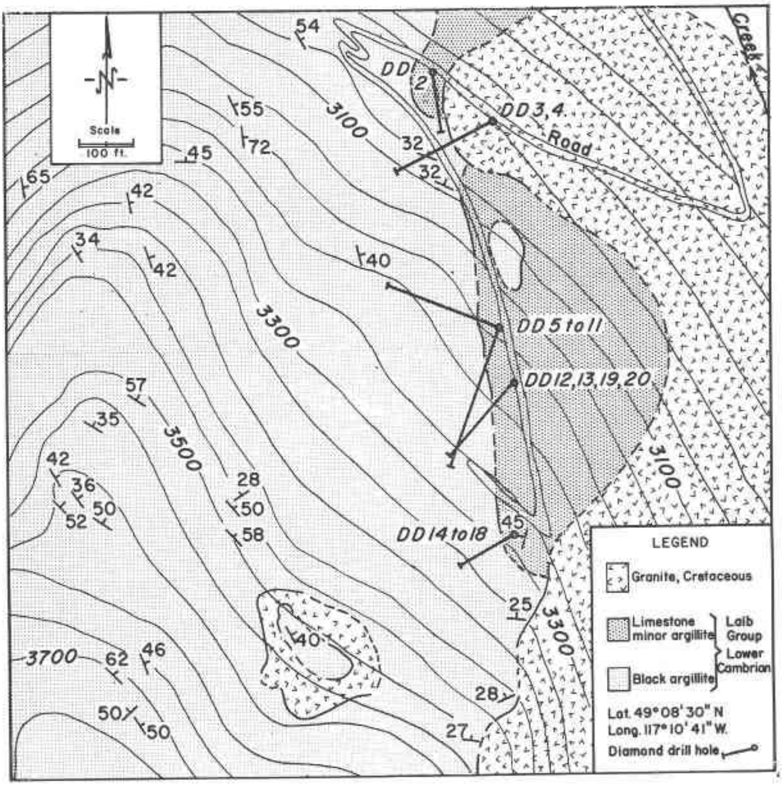

FIG. 2. Geological map of the Victory Tungsten mineral property. Solid geological formation boundaries—observed or certain to within ten feet. Dashed geological formation boundaries—concealed or uncertain by more than ten feet. Contours illustrate the surface topography. Locations and directions of diamond drill holes are shown.

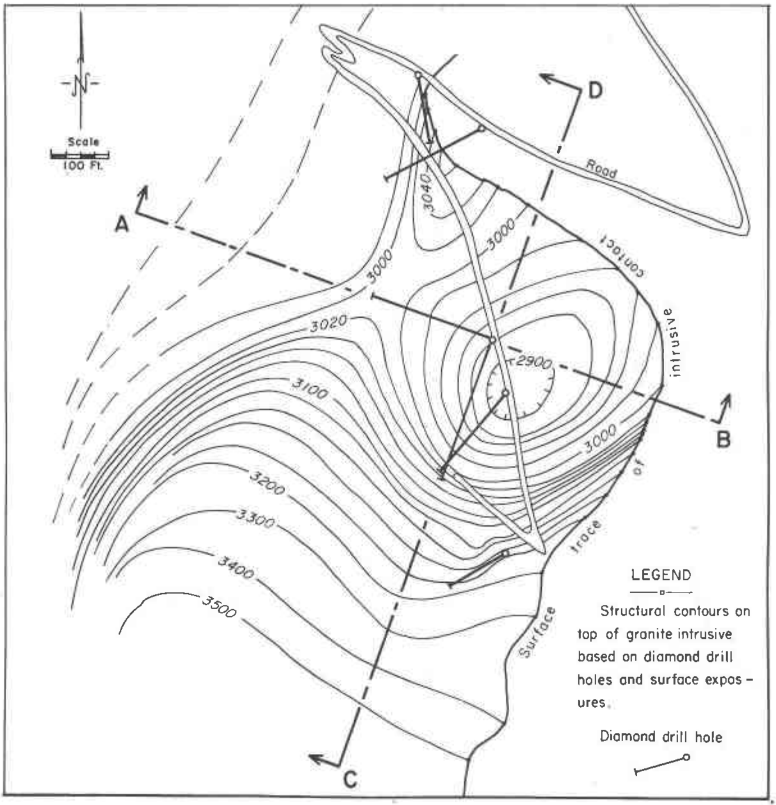

FIG. 3. Structural contour map of the upper surface of the granite intrusive. Contours based on diamond drill results and on observed surface outcrops of granite. Cross-section lines for Figure 4 are shown as A-B and C–D.

is about ten miles north of the Canada-U. S. border and two hundred fifty miles east of Vancouver, British Columbia. It is located on the south side of Sheep Creek three miles east of its confluence with the Salmo River.

Rocks of the lower Cambrian Laib Group have been intruded by granite of the Nelson Intrusives series of approximately mid-Cretaceous age. The Laib Group consists of black argillite and argillaceous limestone, and in the map area of Figure 2 two units from this group are distinguished, a very fine grained black upper unit of argillite showing fairly well developed slaty cleavage, and a lower unit of argillaceous limestone (Little, 1950). Adjacent to the intrusive contact the calcareous rocks have had developed in them a fairly typical suite of contact metamorphic minerals which includes pyrrhotite, pyrite, molybdenite, sphalerite, scheelite, garnet, actinolite, calcite, quartz, and wollastonite.

Figure 2 shows the surface geology, location of access road and positions of the diamond drill holes. Figure 3 shows, at the same scale as Figure 2, contours on top of the granite intrusive as determined from diamond drilling. It can be seen from Figure 3 that the granite is essentially a north-south ridge with a small deep dimple and a pronounced saddle point at its northern end. Most of the pyrrhotite-scheelite mineralization of the property is associated with this hollow in the upper surface of the intrusive body, where it is in contact with the calcareous

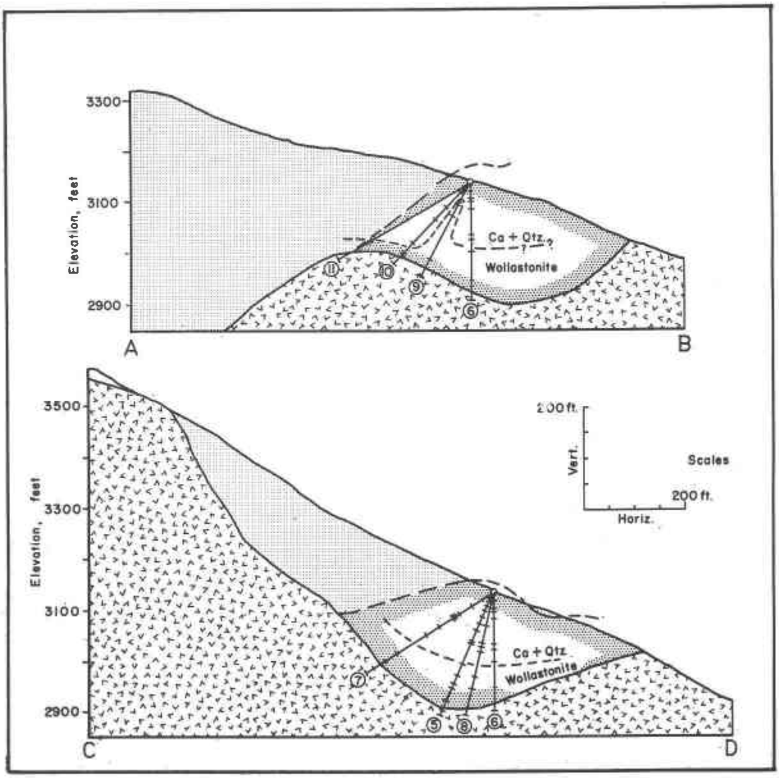

FIG. 4. Cross sections showing the relationships between the rock types and the occurrence of quartz, calcite, and wollastonite. Note the broad parallelism between the wollastonite isograd and the upper surface of the granite. Where the granite is convex upward the isograd is closer, and where it is concave upward the isograd is farther from the granite. Note also the example of extreme divergence from this general regularity shown in the E-W section, where a 'tongue' of wollastonite—bearing rocks extends to a much greater than average distance from the granite. Marks on drill holes show sample locations.

rocks of the Laib Group. Figure 4 illustrates two structural cross sections, the positions of which are shown in Figure 3. Marked on the sections are the locations of the specimens studied for this paper.

The detailed mineralogy of these rocks has not been studied, and will not be reported upon here. The garnet is a grossularite-andradite. Pyrite and pyrrhotite were not observed to coexist in contact, although both occur in the metamorphic aureole. Sphalerite was found in contact with pyrrhotite, but no attempt was made to estimate temperatures from this association. All specimens were examined both optically and with X rays, with particular attention given to the minerals calcite, dolomite, quartz, wollastonite. A number of specimens were found with coexisting calcite and dolomite. The (211) peak of the calcite from these specimens was oscillated against the (111) peak of silicon metal ($2\theta_{111}$ CuKα= 28.466°) as an internal standard. The spacing d_{211} was determined as 3.0268 Å, which corresponds to a temperature of formation of 400°C ± 60°C (Graf and Goldsmith, 1958). This temperature is a minimum, as post-crystallization annealing and exsolution could well have occurred.

Careful examination of thin sections and X-ray diffractometer traces revealed no examples of coexisting calcite, quartz, and wollastonite. The minerals invariably occur either alone or in pairs, suggesting that the three are incompatible throughout most of the rocks examined. The regularity of the distribution of the calcite-quartz-wollastonite minerals illustrated in Figure 4, with the wollastonite always closer to the granite than the assemblage calcite+quartz. It seems that the distribution of the wollastonite was controlled by the granite. No contradictions to the observed zonation were observed in the 72 specimens studied in detail nor in macroscopic examination of all the drill core.

It is not possible to decide to what extent the observed isograd is the result of flow outward of material from the magma and to what extent it is simply the expression of heat flow from the intrusive. Undoubtedly both factors should be considered, and while this can be done qualitatively, a quantitative solution does not seem possible. The pressure that may have prevailed may be estimated from the stratigraphic thickness of the rocks overlying the Laib Group. This thickness is approximately 32,500 feet (Little, 1950), and could have exerted a pressure of about two kilobars. The section is characterized by continuous deposition, with no large unconformities, indicating that most of the section was probably present at the time of intrusion. The pressure estimate is not likely to be in gross error. An uncertainty of 500 bars seems reasonable, although it cannot be supported with detail.

The Nelson intrusives comprise a batholithic mass of more or less granitic rocks exposed over an area of 900 square miles. K-Ar ages on rocks from this mass range from 171 myrs to 49 myrs (Gabrielse and Reesor, 1964). It seems likely that the main episode of emplacement occurred around 170 million years ago. These rocks are variable in both bulk composition and in the proportion of the main minerals, and without a more extensive study it is difficult to place much confidence in any estimate of the liquidus temperature based upon the modal composition. The mode of the granitic rock in the neighbourhood of the area studied here is plagioclase (An_{45}), 10 percent; K-feldspar (microperth), 50 percent; quartz 25 percent; biotite, 8 percent; apatite, hornblende, sphene, magnetite, pyroxene, epidote, chlorite, sericite, totalling 7 percent. Each of these modal percentages varies from place to place by as much as a factor of two, making it clear that the detailed history of the plutonic mass is very complicated. A minimum temperature of the liquidus may be arrived at by referring to experimental data on the system Ab-Or-Qtz-H_2O. At 2000 bars water pressure the 'ternary' liquidus temperature is 700°C. (Tuttle and Bowen, 1958). If the water pressure in the melt were less than the total pressure of 2000 bars than the liquidus temperature would necessarily be higher, so, to the extent that the Ab-Or-Qtz-H_2O system is a good model of the Nelson Intrusives, a minimum temperature for the magma seems to be about 700°C. A more reasonable estimate, perhaps, though not a limiting one, may be obtained from the composition of the plagioclase that coexists with K-feldspar in a rock that appears to have undergone sub-solvus crystalization from the melt. The data of Yoder, Stewart, and Smith (1957) suggest that a temperature of about 770°C might be appropriate. For the purposes of this study it suffices to place the lower limit at 700°C and to entertain the possibility that it might have been as hot as 800°C. In either case the conclusions reached here are not affected, except in the detail of the actual temperature which prevailed.

The intrusive body might be considered to be the upper end of a tabular sheet about 300 meters thick, standing vertically, and extending indefinitely far both downward and horizontally along its length. In view of the local complexity of its surface (Figs. 3 and 4) it would seem unrealistic to base heat flow calculations on this simple model, especially as the phase equilibrium of interest here occurs rather close to the contact. This latter fact suggests that it may be worthwhile to consider a one-dimensional heat flow model with modification for the reentrants and salients on a local scale. This has been done by the use of Figure 1 of Jaeger (1957) with corrections for local irregularities by approximating the reentrants as simple dihedral angles (Jaeger, 1961).

These rough calculations, using 700°C as the intrusive temperature, indicate that the maximum temperature reached at the point where the isograd is most distant from the contact (embayment section, Fig. 4) was approximately 175°C above the local ambient temperature, which may be estimated to be about 270°C at 30°C per km. The final estimated temperature is then about 445°C for this part of the aureole. The place where the isograd comes closest to the contact (Fig. 4, crest of the roof of the granite) may be treated similarly, with a like correction for local irregularity, except for a difference in sign. In this case, at a distance of 15 meters, the maximum temperature excess over the ambient is approximately 180°C, which with the assumed 270°C for the geothermal gradient, results in a temperature maximum of 450°C. If the intrusive temperature was 800°C, both these estimates are raised 40°C. These temperature estimates are rather uncertain both because of the already stated assumptions and because of the additional assumption of purely conductive heat transfer, (no convection in the magma), no transport of heat by moving fluids, and no modification of heat flow by heats of metamorphic reactions. Both estimates are more than the minimum set by the composition of coexisting calcite and dolomite. The two estimates for different parts of the contact are surprisingly close to one another, considering the assumptions, and this may be taken as an indication that the overall regularity of the isograd is due largely to the geometry of the heat flow surface.

The similarity of the two temperature estimates is interesting, and may be used to infer that the equilibrium pressure (Greenwood, 1961) of CO_2 was approximately the same at the two points, and presumably through most of the rock mass. Such equality of equilibrium pressure could be due either to the presence of a H_2O-CO_2 pore fluid of essentially constant composition or to the equilibration of the system with an external reservior of CO_2 at some fixed potential. It seems impossible with the present data to choose between these alternatives.

If the estimate of total pressure is taken seriously, and if the pore fluid were present as a phase consisting entirely of H_2O and CO_2, then a temperature of reaction between 450°C and 500°C requires that the pore fluid be about 95 mol% H_2O and 5 mol% CO_2 (Fig. 1). If the temperature estimate is correct, the fluid could only be pure CO_2 if the total pressure were only about 275 bars, an extreme departure from the estimated pressure.

It seems most reasonable to regard the system as one containing a pore fluid consisting dominantly of H_2O and CO_2 with H_2O being more than ten times as abundant as CO_2. Flow of heat from the granite intrusion reacted the assemblage calcite+quartz to form wollastonite, and the evolved CO_2 was added to the fluid phase. Local additions of extra water from the cooling magma greatly depressed the equilibrium reaction temperature, resulting in prominent salients of the wollastonite assemblage into much cooler rocks. The net effect is that the isograd was controlled by a combination of the temperature and the activity of CO_2. The activity of CO_2 might have been controlled either by the composition of the pore fluid of which it was a part, or by a diffusional equilibrium with some external reservoir or surrounding rocks. Local additions of H_2O, presumably from the crystallizing granite, greatly reduced the activity of CO_2 in some places, permitting the formation of wollastonite at unusually low temperatures.

Summary

Data on the stability of wollastonite in mixtures of H_2O and CO_2 have been presented and the results applied to consideration of a contact metamorphic occurrence. It is shown that the occurrence of the mineral is best explained by reaction induced by flow of heat from the granitic intrusive, and that local variations in the topography of the isograd surface can be accounted for by a combination of the topography of the granite contact and variations in the H_2O content of the pore fluid. The pore fluid, if present as a phase, was apparently less than 10 mol% CO_2. This particular isograd approximates an isotherm of maximum attained temperature in its general shape, but extreme local deviations from this simple condition occur and are most likely caused by variations in the composition of the pore fluid.

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