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CONTACT SKARN FORMATION AT ELKHORN, MONTANA. II: Origin and Evolution of C–O–H Skarn Fluids†

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ABSTRACT: Zoned contact skarns have replaced dolomitic marbles on the upper sides and top of the Black Butte quartz diorite near Elkhorn, Mont. Application of phase equilibria (Bowman and Essene, 1984) and oxygen isotope thermometry to the observed skarn assemblages has fixed temperature of stage I skarn formation at 525° ± 35°C. Similar applications indicate that stage II *Ep* + *Amp* + *Cc* + *Qz* and *Clt* + *Chl* assemblages formed at ⩽ 470° and ⩽ 525°C, respectively. The hydrogen and oxygen isotope compositions of water in equilibrium with stage I skarn and associated igneous and metamorphic rocks at 525°C are:

Intrusion	($\delta^{18}O$ = 7.2 to 8.3; δD = −59 to −53)
Skarn	($\delta^{18}O$ = 7.6 to 12.9; δD = −63 to −54)
Marble	($\delta^{18}O$ = 20.7 to 22.0; δD = −79 to −55)

The isotopic compositions of calcite are:

Metamorphic calcite	($\delta^{18}O$ = 21.6 to 23.8; $\delta^{13}C$ = −2.7 to −1.2)
Skarn calcite	($\delta^{18}O$ = 9.9 to 13.2; $\delta^{13}C$ = −7.8 to −6.0)

Mass-balance calculations indicate that the $\delta^{13}C$ and $\delta^{18}O$ values of skarn calcites cannot result from simple decarbonation of preexisting marble. The carbon and oxygen isotopic data suggest that the skarn calcites formed from fluids that were initially in exchange equilibrium with the Black Butte stock but that became progressively enriched in ^{18}O by exchange with the carbonate wallrock. The calculated hydrogen and oxygen isotope compositions of early, high-temperature (stages I and II) skarn fluids indicate that they contained little or no meteoric water. Replacement of the early, dominantly anhydrous assemblages of stage I by hydrous silicates during stage II was not accompanied by significant influxes of meteoric water. Meteoric water became abundant (⩽ 45 mol percent in stage III) and then predominant (> 70-85 mol percent in stage IV) in later, lower temperature stages of skarn evolution. The close similarity in both hydrogen and oxygen isotope composition between early skarn (stages I and II) and igneous fluids in the Black Butte aureole is consistent with derivation of the skarn fluids from fluids that were equilibrated with isotopically normal igneous rock. The most obvious origin of such fluids is magmatic water that was exsolved during crystallization of the quartz diorite. However, derivation of skarn fluids from certain types of formation water cannot be ruled out. The available geologic, petrologic, and oxygen isotope evidence does suggest

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that, whatever the initial origin of the skarn fluids, these fluids *last* equilibrated with the Black Butte stock.

Systematic increases in the values of $\delta^{18}O$ and in $X(CO_2)$ of the skarn fluid away from the intrusive contact suggest progressive interaction with high-^{18}O carbonate wallrock. Mass-balance calculations suggest that these variations are the result of progressive mixing of water-rich skarn fluids ($\delta^{18}O = 7.5$) with CO_2 ($\delta^{18}O = 30$) evolved during reaction of the fluids with marble. The calculated limits to $X(CO_2)$ agree well with those defined by mineral zonation within the skarns. These calculations provide support for progressive H_2O–CO_2 mixing as a reasonable mechanism for producing the isotopic and mineralogic zonation documented in the Elkhorn skarns.

INTRODUCTION

Hydrogen and oxygen isotope compositions are valuable petrogenetic tracers in a variety of geologic environments (for example, Taylor, 1971, 1974; O'Neil, Fabbi, and Chesterman, 1973; Sheppard and Taylor, 1974). Shieh and Taylor (1969) made the first isotopic study of contact replacement skarns and showed that skarn calcite was significantly depleted in ^{13}C and ^{18}O relative to the marble precursor. The authors proposed that this depletion was the result of evolution of CO_2 enriched in ^{13}C and ^{18}O during the replacement of marble by skarn. Taylor and O'Neil (1977) demonstrated that the large difference in carbon and oxygen isotope compositions between igneous rocks and marble allows tracking of the progressive interaction between skarn fluid and carbonate wallrock as well as estimating $X(CO_2)$ values in oxidized C–O–H skarn fluids. Rye, Hall, and Ohmoto (1974) showed that progressive water-rock interaction is evidenced in carbonate rocks by systematic carbon and sulfur isotope variations as well. These studies show clearly that stable-isotope data can provide important information on progressive water-rock interaction, fluid sources, and especially compositional variables like $f(O_2)$, $X(CO_2)$, $f(S_2)$, pH, et cetera, *if* sufficient temperature control can be established by carefully integrated petrologic and isotopic studies.

Integrated petrologic-stable isotope studies have been conducted on the zoned Ca–Al–Si–Mg(Fe) contact replacement skarns and associated igneous and metamorphic rocks in the Black Butte stock aureole near Elkhorn, Mont. Geologic relations, mineral zonation and compositions, and physical-chemical conditions of formation are discussed in part I (Bowman and Essene, 1984). In this study we report carbon, hydrogen, and oxygen isotopic analyses of mineral samples from the skarns as well as associated igneous and metamorphic rocks. With the temperature control made possible by the associated petrologic studies, these data provide constraints on sources of skarn fluids and allow some insight to be made into the roles of compositional variables and processes of fluid-wallrock interaction in skarn petrogenesis. The mineralogically variable and zoned skarns at Elkhorn are a particularly appropriate site for application of the H_2O–CO_2 model of Taylor and O'Neil, because independent petrologic evidence (Bowman and Essene, 1984) suggests that variations in $X(CO_2)$ may have been important in producing the observed mineralogical variations.

SUMMARY OF GEOLOGICAL AND PETROLOGIC RELATIONSHIPS

The Black Butte stock, one of several small diorite/quartz–diorite stocks representative of an early mafic phase of the Boulder Batholith, intrudes and metamorphoses a late Precambrian to Paleozoic sequence of dolomites, with mudstone and minor calc–pelite at Elkhorn, Mont. (Klepper, Weeks, and Ruppel, 1957). Mineralogically zoned magnesian skarns are extensively developed in the dolomite marbles on the upper sides and top of the Black Butte stock (fig. 1). The geology of the Elkhorn, Mont. area, and the petrology, zoning, and physical-chemical conditions of skarn formation were presented previously (Klepper, Weeks, and Ruppel, 1957; Bowman and Essene, 1984) and will not be given in detail here.

With regard to this study, several aspects of skarn formation should be noted. Skarn development occurred in at least four time stages. The initial stage of skarn development (I) is characterized by a variety of three-phase and less often four-phase assemblages which usually include garnet and pyroxene, and occasionally epidote, vesuvianite, clintonite, amphibole, or spinel. This stage constitutes greater than 90 percent by volume of the exposed skarn in the area. Stage II was marked by the local replacement of garnet and pyroxene by combinations of epidote, amphibole, biotite, clintonite, chlorite, calcite, and quartz. Stage III consisted of the minor development of axinite-bearing quartz veins with epidote, chlorite, and calcite. Stage IV consisted of fracturing and shearing of earlier formed skarn and replacement by chlorite and serpentine along these shear zones.

The stage I skarns consist dominantly of grandite garnet plus diopsidic pyroxene (with variable and often significant amounts of tschermaks and hedenbergite components), often with minor calcite and accessory sphene, apatite, and less commonly magnetite. The stage I skarns are mineralogically variable and unusual in that they contain vesuvianite, epidote, clintonite, and rarely, amphibole associated with, but not replacing, garnet and pyroxene. These occurrences contrast sharply with the more typical replacement mode of occurrence that characterizes these hydrous silicates in the later stages of skarn development at Elkhorn and in most skarns. Bowman and Essene (1984) assigned to stage I minerals that were not found in voids, veins, or fractures and where these minerals are closely associated with garnet and/or pyroxene, without evidence of replacement. These minerals are assumed to be contemporaneous and in a state of thermal equilibrium; textural and other evidence supporting this assumption are given by Bowman and Essene (1984). It is further assumed that these mineral assemblages formed in isotope exchange equilibrium. This assumption is supported by the consistent order of ^{18}O-enrichment among the minerals of the skarns and stock. However, the assumption is inherently difficult to test in skarns because of their high variance and because the oxygen isotope properties of many of the major minerals found in magnesian skarns (for example, vesuvianite, clintonite, spinel) are not well known.

The stage I skarns are zoned mineralogically on several scales, and three major zonation types — Massive, Contact, and Nodule — have been

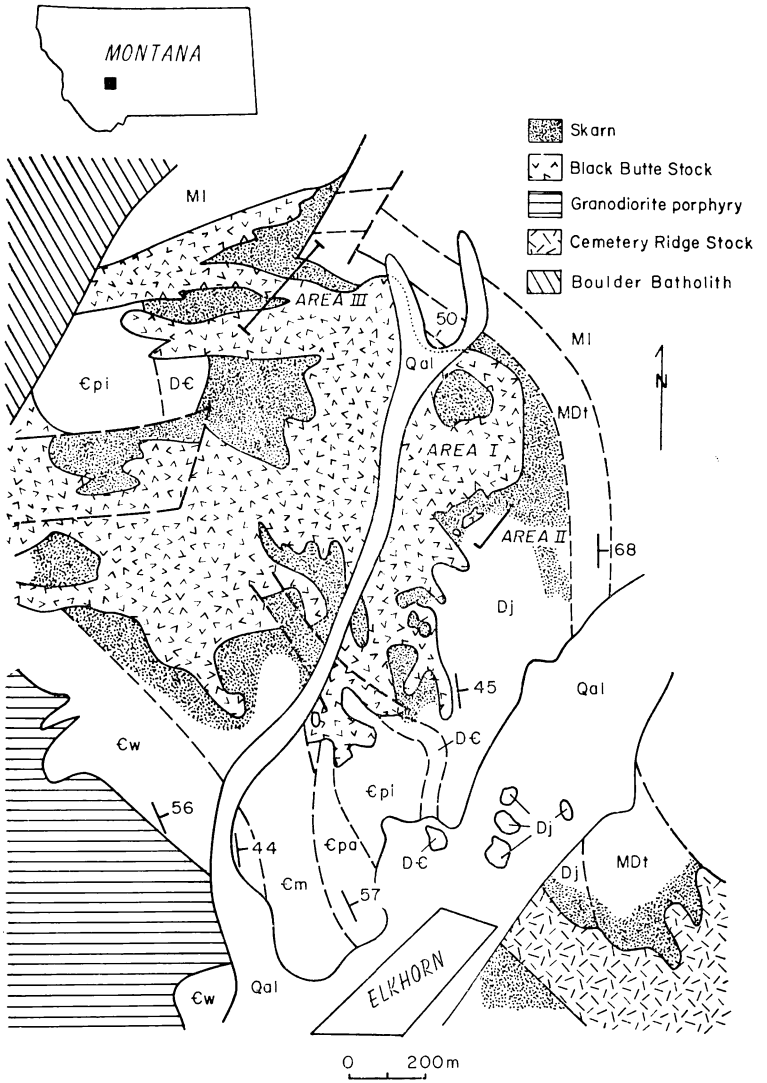


Fig. 1. Geologic map of the Black Butte contact aureole (modified from Klepper, Weeks, and Ruppel, 1957) illustrating geologic relations between the Black Butte quartz-diorite, contact replacement skarns, and surrounding country rock. Most of the country rock is carbonate (dolomite), with the exceptions of the Park (Cpa), Wolsey (Cw), and Three Forks (MDT) shales. Other formation abbreviations are Cm = Meagher limestone, Cpi = Pilgrim dolomite, DC = Red Lion formation, Dj = Jefferson dolomite, Ml = Lodgepole limestone, Qal = alluvium. Areas I to III are discussed in the text. Heavy lines are faults, dashed where approximately located. The Black Butte stock is irregular in outcrop geometry, displaying numerous reentrants and several roof pendants of variable size. These localities are sites for extensive development of massive garnet-pyroxene skarns. The attitude of the igneous contact can fluctuate from nearly vertical to sub-horizontal over small distances. Skarn is developed at the igneous contact to a maximum of about 120 m below the elevation of the highest preserved skarn. These features suggest that present exposures are in the uppermost parts of the intrusion.

distinguished (see table 2 in Bowman and Essene, 1984). The Massive zoned skarns constitute most of the exposed skarn masses in the Black Butte aureole. The zoned skarns can be grouped into five zones, spatially arranged with increasing distance from the igneous contact (Bowman and Essene, 1984):

Zone A: *Px* + *Ep* ± *Sc* ± *Cc* (Contact skarn)
Zone B: *Gn* + *Px* + *Vs* ± *Cc*
Zone C: *Gn* + *Px* + *Cc*; absence of *Vs* and *Sp*
Zone D: *Gn* + *Px* + *Pg* ± *Cc* or *Gn* + *Px* + *Sp* ± *Clt* ± *Cc*
Zone E: *Px* or *Px* + *Sp* ± *Cc* or *Px* + *Pg* ± *Cc*; absence of *Vs* and *Gn*

Four of the zones (B to E) are sufficiently large and coherent to be mappable on the east and northeast sides of the stock (fig. 2).

Bowman and Essene (1984) interpreted these various skarn zones to be broadly contemporaneous but with zone boundaries migrating outward from the igneous contact through time. Although there is no compelling evidence to rule out sequential formation of some of the skarn zones, the available information from phase equilibria suggests that the zones formed under near-isothermal conditions (Bowman and Essene, 1984). Thus, for the purposes of this paper, we will assume that the various skarn zones were broadly contemporaneous and formed under approximately isothermal conditions, recognizing that this interpretation could be a simplification.

Based on applications of experimental and calculated phase equilibria to observed skarn assemblages, Bowman and Essene (1984) estimated the P-T conditions of stage I skarn formation to be P = 1.0 ± 0.3 kb and T = 525° ± 35°C. Stage II probably formed at similar (for example, 525°C) to somewhat lower temperature (T ⩽ 470°C), based on the presence of *Clt* + *Chl* and *Ep* + *Amp* + *Cc* + *Qz* assemblages, respectively. Phase equilibrium considerations of the zoned mineralogy of the Massive skarns suggest that the zoning could be the result of a near-isothermal increase in $X(CO_2)$ from 0.03 to 0.07 at the igneous contact to approx 0.30 ± 0.05 at the skarn-marble interface. One objective of this study is to determine if the oxygen-isotope evidence is consistent with such an increase.

ANALYTICAL RESULTS

Analytical results for minerals and modern meteoric water from the area are given in tables 1, 2, and 3. All data are given in the δ-notation. All δ-values are given in permil relative to SMOW for oxygen and hydrogen (Craig, 1961b) and PDB for carbon (Craig, 1957). Mineral zones from which the skarn samples were taken are identified by letter. The distribution and mineralogy of these zones were summarized previously (see tables 1 and 2 in Bowman and Essene, 1984) and illustrated in figure 2. Tables 1 to 3 also contain calculated $\delta^{18}O$ and δD values of water that would have been in equilibrium with the analyzed minerals at the relevant temperatures. Chemical analyses of hydrous silicates used in the calculation of δD values of H_2O are compiled in Bowman (ms) and

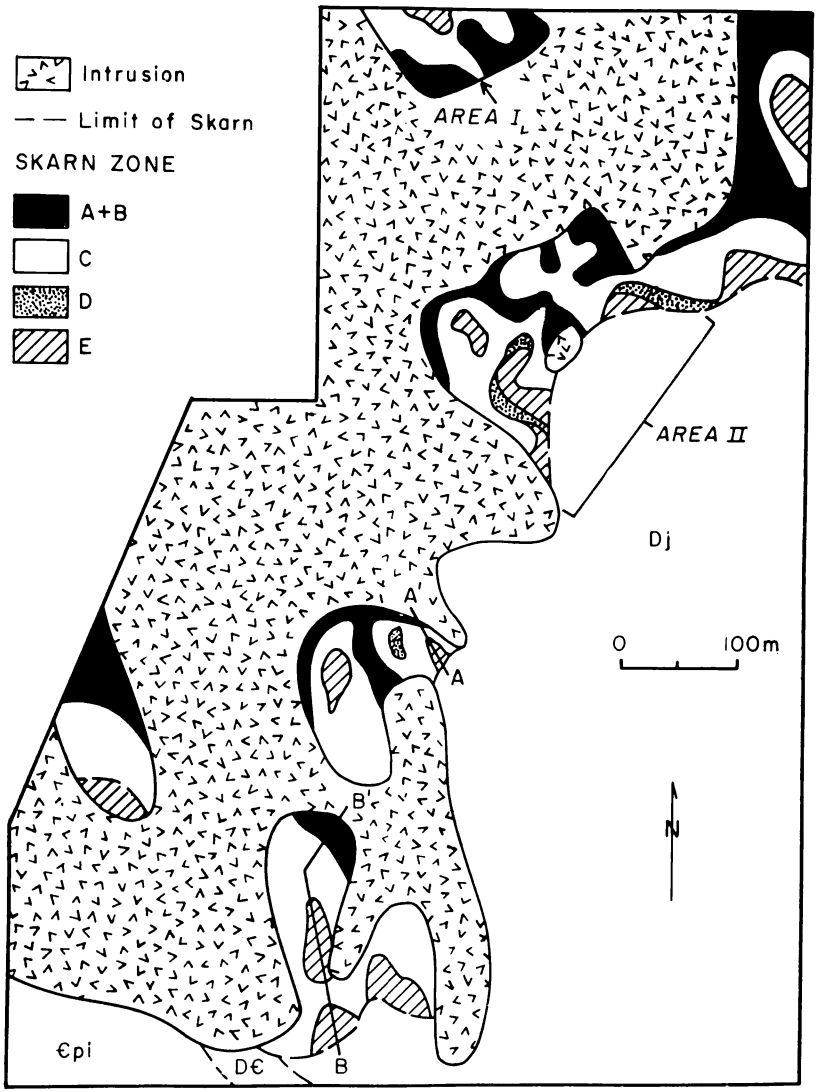


Fig. 2. Geologic map of the eastern portion of the Black Butte aureole, summarizing the distribution of the predominant mineral zones of the Massive skarns (see table 2, Bowman and Essene, 1984). The mineral zones plotted in any area are the dominant mineralogies of the skarns. Fine-scale variations in mineralogy and irregularities in zone boundaries have not been plotted to emphasize general skarn zonation patterns. The letters designate each mineral zone as defined in the text: A = *Px* + *Ep* ± *Sc* ± *Cc*; B = *Gn* + *Px* + *Vs* ± *Cc*; C = *Gn* + *Px* + *Cc*, absence of *Vs* and *Sp*; D = *Gn* + *Px* + *Pg* ± *Cc* or *Gn* + *Px* + *Sp* ± *Clt* ± *Cc*; E = *Px* or *Px* + *Sp* ± *Cc* or *Px* + *Pg* ± *Cc*, absence of *Gn* and *Vs*. Detailed sampling was conducted in areas I, II, and III (fig. 1) and along traverses A-A′ and B-B′.

Bowman and Essene (1984). The fractionation factors used to calculate the isotopic compositions of coexisting fluids and for oxygen isotope geothermometry are from O'Neil and Taylor (1967), Clayton, O'Neil, and Mayeda (1972), O'Neil, Clayton, and Mayeda (1969), Bottinga and Javoy (1973, 1975), and Suzuoki and Epstein (1976). Oxygen and hydrogen isotope data for the Black Butte stock and skarns are plotted as a function of distance from the intrusive contact in figures 3 and 4.

Oxygen isotope compositions in the Black Butte stock.—Igneous minerals have $\delta^{18}O$ values typical of basic to intermediate igneous rocks (Taylor, 1974) and the relative ^{18}O-enrichments among the unaltered igneous minerals are normal: quartz > plagioclase > amphibole ≅ biotite. These relations suggest a reasonably close approach to isotopic exchange equilibrium. None of the samples analyzed has unusually low $\delta^{18}O$ or anomalous Δ-values for quartz–plagioclase pairs as would be characteristic of plutons that have interacted extensively with isotopically light meteoric water (Taylor, 1974).

The $\delta^{18}O$ values of plagioclase and amphibole correlate with igneous mineralogy and proximity to the igneous contact. The $\delta^{18}O$ values of plagioclase appear to decrease with anorthite content and increase with the abundance of quartz. As a result, the $\delta^{18}O$ values of plagioclase from the diorite are typically about 1 permil lower than those of plagioclase from the quartz diorite. However, of the total 1.5 permil variation measured in plagioclase, only about 0.6 permil can be due to the variation in anorthite content (An_{35}-An_{65}) even at temperatures as low as 525°C (O'Neil and Taylor, 1967). The rest of the variation must be due to such factors as variation in the $\delta^{18}O$ value of the primary magmas, crystal fractionation effects, or interaction with high $\delta^{18}O$ country rock.

Samples of plagioclase and amphibole collected within 8 m of the igneous contact are up to 1.5 and 0.8 permil heavier, respectively, than their counterparts in the stock interior (fig. 3). The maximum ^{18}O-enrichment occurs in the dehydrated *Px* + *Pg* zone (endoskarn) which constitutes the outermost 2 to 60 cm of the intrusion (table 1). The local ^{18}O-enrichments are similar to those found in stock margins in several other studies (Shieh and Taylor, 1969; Turi and Taylor, 1971; Taylor and O'Neil, 1977) and are likely the result of chemical interaction and isotopic exchange with the high ^{18}O carbonate country rock. Bulk chemical and petrographic data (Bowman, ms) are consistent with this interpretation.

The oxygen isotope temperatures based on plagioclase–amphibole and quartz–plagioclase fractionations and the thermometry equations of Bottinga and Javoy (1973, 1975) are 490° to 680°C (with one exception, 760°C) and 690° to 870°C for the quartz diorite and diorite phases, respectively. Application of thermometry equations which incorporate the experimental data for quartz (Clayton, O'Neil, and Mayeda, 1972; Matsuhisa, Goldsmith, and Clayton, 1979) yields temperatures from quartz–plagioclase fractionations that are 120° to 175°C lower. Sub-solidus isotopic exchange on cooling is suggested for both igneous phases, but

TABLE 1

Hydrogen and oxygen isotope data and descriptions of samples from the Black Butte stock, endoskarn, and contact endoskarn

Sample*	Rock Type or Mineral Assemblage	Mineral** $\delta^{18}O$ (δ D)				Calculated† H_2O, 525°C		Oxygen Isotope‡ Temperature, °C
		Pg	Amp	Bi	Qz	$\delta^{18}O$	δD	
BLACK BUTTE STOCK								
X1-5 (5)	Quartz Diorite	+8.7	+6.3 (-90)		+11.1	+8.1	-59	520 (Qz-Amp) 490 (Qz-Pg) 540 (Pg-Amp)
X1-8 (20)	Diorite	+7.5	+6.0 (-87)			+7.2	-56	800 (Pg-Amp)
X1-9 (70)	Diorite	+7.6	+5.9 (-93)			+7.2	-53	710 (Pg-Amp)
X1-10 (3.5)	Quartz Diorite	+8.9	+6.8 (-87)		+10.9	+8.3	-55	580 (Qz-Pg) 700 (Qz-Amp) 620 (Pg-Amp)
X2-5 (80)	Diorite	+7.4	+6.0			+7.2		870(Pg-Amp)
E1-4 (1.5)	Diorite	+7.9	+6.4 (-92)			+7.6	-58	800 (Pg-Amp)
E2-67 (210)	Diorite	+7.6	+5.8 (-88)			+7.2	-59	690 (Pg-Amp)
E3-18 (7)	Diorite	+7.7	+6.0 (-77)			+7.3	-53	710 (Pg-Amp)
E3-22 (1)	Quartz Diorite	+8.9	+6.5 (-88)		+10.8	+8.3	-57	680 (Qz-Amp) 590 (Qz-Pg) 540 (Pg-Amp)
E6-20 (9)	Diorite	+7.6	+6.0 (-89)			+7.3	-54	760 (Pg-Amp)
E7-20 (8)	Quartz Diorite	+8.6	+6.4 (-85)	+6.4 (-95)	+11.0	+8.0	-53	540 (Qz-Amp) 500 (Qz-Pg) 580 (Pg-Amp)
E11-43 (180)	Quartz Diorite	+8.5	+6.6			+7.9		650 (Pg-Amp)

ENDOSKARN		Pg	Px				
C5-10 (0.1)	Px + Pg	+9.3	+7.2			+8.2	420 (Pg-Px)
C5-15 (0.2)	Px + Pg + Amp		+7.0			+8.0	
E11-4a (0.6)	Px + Pg	+8.6	+7.2			+8.0	550 (Pg-Px)
E11-4b (0.4)	Px + Pg	+9.1	+7.4			+8.2	490 (Pg-Px)
E11-4c (0.1)	Px + Pg	+9.6	+7.7			+8.5	440 (Pg-Px)
CONTACT EXOSKARN		Pg	Gn	Px	Ep		
E11-4d (0.1)	Px + Gn		+8.2	+7.8		+8.8	
C10-38 (0.2)	Px+Gn+Pg+Ep+Cc	+9.1		+7.5	+8.0 (-45)	+8.5	530 (Pg-Px)
C17-28 (0.1)	Px + Gn +Ep			+9.8		+10.8	

* The number in parentheses is the distance in meters to intrusive contact.

** Mineral abbreviations: *Pg* — plagioclase; *Amp* — amphibole; *Bi* — biotite; *Qz* — quartz; *Gn* — garnet; *Px* — pyroxene; *Ep* — epidote; *Cc* — calcite.

† Hydrogen isotope compositions of H_2O in equilibrium with the hydrous silicates were calculated using the data from Suzuoki and Epstein (1976). Octahedral site compositions in the hydrous silicates were determined by electron microprobe analysis (Bowman, ms). Oxygen isotope compositions of H_2O were calculated at 525°C with modal analyses and the mineral H_2O fractionation factors compiled in Friedman and O'Neil (1977).

‡ Error due to analytical uncertainty alone is, on average: Qz–Amp, ± 20°C; Pg–Amp, ± 45°C; Pg–Px, ± 50°C; and Qz–Pg, ± 35°C for $T < 500$°C and ± 50 for $T > 600$°C.

TABLE 2

Carbon, hydrogen, and oxygen isotope data and description of samples from the Massive skarns

Sample*	Rock Type or Mineralogy	Mineral** $\delta^{18}O$ (δD)[$\delta^{13}C$]					Calculated H_2O† 525°C		Oxygen Isotope‡ Temperature, °C
		Gn	Px	Amp	Ep, Pg or Clt	Cc	$\delta^{18}O$	δD	
ZONE§ B									
C1-29 (6)	Gn+Px+Vs+Clt	+9.4	+8.0		(-77)(Clt)		+9.0	-57	
C1-32 (0.7)	Gn+Ep+Amp+Cc			+7.4 (-79)	+8.0(Ep) (-56)	+10.2 [-7.1]	+8.8	-56	
C1-40 (5)	Gn+Px+Vs+Cc	+8.3	+8.1			+10.7 [-6.1]	+9.1		595 (Cc-Px)
C2-29 (0.5)	Gn+Ep+Amp+Cc			+7.6 (-76)		+10.5 [-7.3]	+9.2	-55	
C2-30 (1.0)	Gn+Ep+Amp+Cc+Qz	+8.8		+8.3 (-80)	+8.1(Ep) (-60)		+9.8	-56	
C13-12 (1.5)	Gn+Px+Pg+Ep+Cc		+8.0		+9.5(Pg)		+9.0		550 (Pg-Px)
E1-35 (3.3)	Gn+Px+Vs+Clt+Cc		+8.0		+8.4(Clt) (-75)	+11.4 [-6.0]	+9.0	-62	450 (Cc-Px)
X1-6 (4)	Gn+Px+Vs+Cc	+8.3	+8.9				+9.9		
X2-10 (2)	Gn+Px+Vs+Cc	+9.1	+9.7				+10.7		
X2-13 (3)	Gn+Px+Vs+Cc		+9.8				+10.8		
ZONE C									
C10-36 (3)	Gn+Px; retro Amp (Stage II)		+7.7	+8.0 (-78)			+8.6 (+8.7)	(-58)	
E1-29 (1)	Gn+Px+Cc		+8.1				+9.1		
E2-50 (2)	Gn+Px+Cc; retro. Amp (Stage II)	+8.2	+7.8	+7.6 (-82)		+10.8 [-6.6]	+8.9 (+8.3)	(-61)	510 (Cc-Px)
E2-52 (0.5)	Gn+Px+Cc; retro. Amp (Stage II)	+7.6	+6.9	+7.1 (-81)		+10.1 [-6.3]	+7.9 (7.8)	(-61)	480 (Cc-Px)
E2-53 (1.0)	Gn+Px+Cc; retro. Amp (Stage II)	+7.3	+7.0	+7.3 (-84)			+8.0 (+8.0)	(-64)	
E2-59 (2)	Gn+Px+Cc; retro. Clt (Stage II)		+8.3		+8.1(Clt) (-79)		+9.3 (+8.8)	(-63)	

E3-78 (12)	Gn+Px+Cc+Qz	+9.1	+8.8			+11.8 [-7.6]	+9.9		510 (Cc-Px)
E3-81 (6)	Gn+Px+Cc		+8.8			+11.2 [-7.4]	+9.8		630 (Cc-Px)
E9-23 (1)	Gn+Px+Cc; retro. Amp (Stage II)	+6.7	+6.9	+6.9 (-84)			+7.9 (+7.6)	(-54)	
E9-46 (7)	Gn+Px+Cc; retro. Amp (Stage II)		+8.6	+9.0 (-82)			+9.6 (+9.7)	(-63)	
C11-18 (3)	Gn+Px+Cc; retro. Amp (Stage II)	+10.4	+9.5	+10.0 (-87)		+12.2 [-7.2]	+10.5 (+10.7)	(-57)	570 (Cc-Px)
ZONE D									
C12-31a (9.5)	Gn+Px+Clt+Sp+Cc		+8.9		+8.4(Clt)	+12.1 [-6.9]	+9.9	-59	480 (Cc-Px)
C12-37b (12)	Gn+Px+Clt+Sp+Cc		+9.2		+8.9 (Clt) (-83)		+10.2	-63	
E2-56a (2.5)	Gn+Px+Pg		+7.4		+9.4(Pg)		+8.4		430 (Pg-Px)
E3-90 (3)	Gn+Px+Pg	+8.9	+8.1		+9.9(Pg)	+10.6 [-6.8]	+9.3		470 (Pg-Px) 620 (Cc-Px)
E3-91 (3)	Gn+Px+Pg		+8.6		+10.3(Pg)		+9.7		490 (Pg-Px)
E9-37b (1.5)	Gn+Px+Pg	+7.1	+7.1		+9.0(Pg)	+9.9 [-7.2]	+8.3		440 (Pg-Px) 550 (Cc-Px)
ZONE E									
E2-1 (21)	Pg+Pg+Cc		+12.2		+13.2(Pg)		+13.2		660 (Pg-Px)
E2-2 (19)	Px+Cc		+10.9			+13.2 [-6.9]	+11.9		680 (Cc-Px)
E2-5 (18)	Px+Sp+Clt+Cc		+10.7				+11.7		
E2-9 (11)	Px+Sp+Clt+Cc		+10.4				+11.4		
E2-10 (13.5)	Px+Sp+Clt+Cc		+10.3		(-79)(Clt)		+11.3	-62	
E2-13 (8)	Px+Cc; retro. Clt (Stage II)		+8.5		+8.3(Clt) (-82)		+9.3 (+9.0)	(-58)	

TABLE 2 (continued)

ZONE E (continued)									
E3-34 (8.5)	Px+Cc; retro. Clt (Stage II)		+8.9		+7.8(Clt) (-107)	+12.0 [-7.6]	+9.9 (+8.6)	(-92)	495 (Cc-Px)
E8-90 (7)	Px+Sp+Cc		+9.0				+10.0		
E10-43 (5)	Px+Fo+Sp+Chl+Cc		+8.7		+8.5(Chl) (-89)	+11.0 [-7.6]	+9.7	-67	680 (Cc-Px)
C11-7a (1)	Px+Sp+Clt+Cc		+8.7		+8.1(Clt) (-80)		+9.7	-60	
C11-16 (1.5)	Px+Clt+Cc		+9.0				+10.0		
C11-17 (2)	Px+Cc; retro. Amp (Stage II)		+9.2	+9.4 (-76)		+12.4 [-6.6]	+10.3 (+10.1)	(-54)	480 (Cc-Px)
C11-21 (2.5)	Px+Cc; retro. Amp (Stage II)		+9.0	+9.2 (-79)			+10.0 (+9.9)	(-60)	
C12-26 (13)	Px+Cc; retro. Amp (Stage II)		+8.8	+8.5 (-93)		+11.6 [-7.8]	+9.9 (+9.3)	(-75)	550 (Cc-Px)
STAGE III		Chl	Srp	Ep					
C13-4	Chl+Cc+Qz+Ax+Ep	+6.3) (-136)					+8.8	-92	
C16-56	Chl+Cc+Qz+Ax+Ep	+6.8 (-130)		+9.9 (-88)			+9.3	-88	
E3-100	Chl+Cc+Qz+Ax+Ep			+7.5 (-71)			+6.9	-71	
STAGE IV									
E1-33	Chl and/or Srp	+5.8 (-160)					+7.2	-130	
E2-23	Chl and/or Srp	(-155)						-125	
E3-36	Chl and/or Srp		+5.2 (-172)				+6.4	-146	
E10-40	Chl and/or Srp		(-158)					-132	

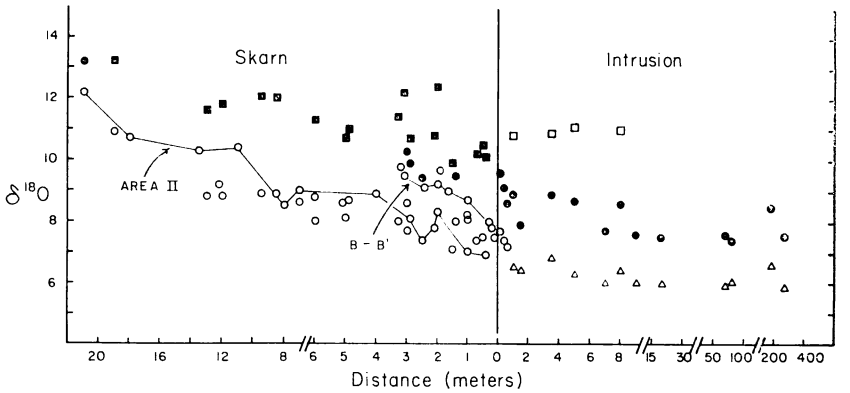


Fig. 3. Plot of the $\delta^{18}O$ values of minerals from the Black Butte stock and skarns as a function of distance from the intrusive contact. Samples are predominantly from areas I through III (see figs. 1 and 2). Samples collected on detailed traverses (B-B', area II) are connected by lines for illustrative purposes. Mineral symbols are: pyroxene (open circles); plagioclase (solid circles); quartz (open squares); amphibole (open triangles); calcite (solid squares).

the effects are more significant and pervasive in the quartz–diorite, especially if the experimentally-based quartz–plagioclase equations are considered. However, obvious alteration features like clouded or sericitized feldspars, chloritized or epidotized pyroxenes and amphiboles, or deuteric veins are very rare.

Oxygen and carbon isotope compositions of marble and skarn carbonates.—The $\delta^{18}O$ values of calcite from the unmetasomatized dolomitic marbles vary from 21.6 to 23.8, averaging 22.9 permil, and dolomites from the low-grade marble and unmetamorphosed sedimentary dolostone have $\delta^{18}O$ values from 23.0 to 24.6 (table 3). All these values are typical for marine carbonates of Cambrian through Devonian age (Keith and Weber, 1964; Veizer and Hoefs, 1976). There is no apparent correlation between $\delta^{18}O$ values of calcite and metamorphic grade. The marble is slightly, but systematically, depleted in both ^{18}O and ^{13}C (< 2 permil) relative to unmetamorphosed dolostone. These small differences are most likely the result of low-temperature (< 400°C) metamorphic devolatilization reactions. At Elkhorn, phlogopite plus calcite assemblages occur in marbles below the tremolite isograd resulting from the reaction:

$$3\ \mathrm{Dol} + \mathrm{Kfs} + \mathrm{H_2O} = \mathrm{Ph} + 3\ \mathrm{Cc} + 3\ \mathrm{CO_2}\,. \qquad (1)$$

← * The number in parentheses is the distance in meters to igneous contact.

** Mineral abbreviations: *Gn* — garnet; *Px* — pyroxene; *Amp* — amphibole; *Ep* — epidote; *Pg* — plagioclase; *Chl* — chlorite; *Srp* — serpentine; *Clt* — clintonite; *Cc* — calcite; *Vs* — vesuvianite; *Sp* — spinel; *Qz* — quartz; *Ax* — axinite.

† Hydrogen and oxygen isotope compositions in parentheses are those of Stage II fluid.

‡ Error due to analytical uncertainty alone is, on average: Cc–Px, ± 35°C; Pg–Px, ± 50°C.

§ Individual zones are described in the text.

TABLE 3

Carbon, hydrogen, and oxygen isotope data and description of samples from marbles, sedimentary dolostone and modern meteoric water in the Black Butte aureole

Sample*	Mineralogy	Mineral**$\delta^{18}O$[δ D]($\delta^{13}C$)				Calculated H_2O† 525°C	
		Cc	Dol	Qz	Amp, Chl or Bi	$\delta^{18}O$	δ D
MARBLE							
C4-1 (240)	Dol+Qz		+22.5 (-2.1)	+15.2		+20.5	
C4-3 (240)	Dol+Cc+Amp	+22.3 (-1.7)			[-93](Amp)	+20.8	-79
E2-2a (0.01)	Dol+Cc+Fo	+19.2 (-1.5)				+17.7	
E2-2b (0.02)	Dol+Cc+Fo	+21.6 (-1.6)				+20.0	
E2-2c (0.03)	Dol+Cc+Pe(Br)+Fo	+23.6 (-1.4)				+22.1	
E2-2d (0.05)	Dol+Cc+Pe(Br)+Fo	+24.1 (-1.3)				+22.6	
E2-2e (0.06)	Dol+Cc+Pe(Br)+Fo	+23.2 (-1.2)				+21.7	
E2-2f (0.07)	Dol+Cc+Pe(Br)+Fo	+23.8 (-1.5)				+22.3	
E2-2g (0.1)	Dol+Cc+Pe(Br)+Fo	+23.4 (-1.6)				+21.9	
E2-2,Ave(b-g)	Dol+Cc+Pe(Br)+Fo	+23.2 (-1.4)				+21.7	
E2-62 (120)	Dol+Qz+Bi		+23.1 (-2.2)	+15.4	+19.6(Bi) [-97]	+21.1	-78
E2-80 (90)	Dol+Qz			+16.6			
E3-1 (3)	Cc+Pe(Br)+Dol	+23.8 (-1.2)				+22.3	

E3-25 (80)	Dol		+21.6 (-2.6)			+19.6	
E3-60 (70)	Dol+Qz			+15.3			
E3-65 (40)	Dol+Cc+Amp+Fo				+20.5(Amp) [-72]	+22.0	-60
E3-66 (30)	Dol+Chl	+22.8 (-1.3)			[-65](Chl)	+21.3	-55
E3-70 (20)	Dol+Cc+Fo+Sp	+23.2 (-2.5)				+21.7	
E5-1 (5)	Dol+Cc+Pe(Br)+Fo	+23.5 (-2.6)				+22.0	
E5-10 (100)	Dol+Cc+Amp+Fo	+22.2 (-2.7)			+20.7(Amp) [-93]	+20.7	-75
	SEDIMENTARY DOLOSTONE						
Cpi-3			+23.0 (-1.7)				
Dj-4			+24.6 (-1.3)				
Dj-7			+24.0 (-2.1)				
	MODERN METEORIC WATER						
Elkhorn Spring						-19.4	-147
Slaughterhouse Gulch						-19.4	-147

* The number in parentheses is the distance in meters from intrusive or skarn contact.

** Mineral abbreviations: *Amp* — amphibole; *Bi* — biotite; *Chl* — chlorite; *Qz* — quartz; *Fo* — forsterite; *Sp* — spinel; *Pe* — periclase; *Br* — brucite; *Cc* — calcite; *Dol* — dolomite.

† Hydrogen and oxygen isotope compositions of H_2O were calculated as described in table 1 and the text.

This assemblage and the apparent presence of fluids with high $X(CO_2)$ (Bowman and Essene, 1982) indicate that significant quantities of CO_2 were generated within the marbles below the tremolite isograd. However, the small amount of ^{18}O- or ^{13}C-depletion and absence of progressive lowering of $\delta^{18}O$ and $\delta^{13}C$ values with increasing metamorphic grade suggest that relatively little ^{18}O- and ^{13}C-enriched CO_2 was evolved during prograde metamorphism above 400°C.

Void-filling chalcedony lenses in unmetamorphosed dolostones and low-grade marbles have $\delta^{18}O$ values of 15.2 to 16.6 (table 3) and are out of isotopic equilibrium with the carbonate host, probably because they are post-depositional precipitates that formed at low temperatures (< 150°C) from formation or meteoric water. Quartz is exhausted in the initial metamorphic reactions. At intermediate to high metamorphic grades (above the tremolite isograd), the two oxygen isotope analyses of amphibole have $\Delta(Cc\text{-}Amp)$ values of 2 to 5 permil. These values are consistent with those observed elsewhere (Shieh and Taylor, 1969; Taylor and O'Neil, 1977) for similar metamorphic grades.

The depletion of ^{18}O and ^{13}C in skarn calcite relative to metamorphic calcite is striking. The $\delta^{18}O$ values of skarn calcites vary widely from 9.9 to 13.2 permil but are significantly lower than the average value of 22.9 measured for metamorphic calcite. The $\delta^{18}O$ values of the skarn calcites increase with increasing distance of the sample from the igneous contact (fig. 3). The $\delta^{13}C$ values of carbonates (−7.8 to −6.0 permil) are similar to those of presumed magmatic origin (Taylor, Frechen, and Degens, 1967; Deines, 1970; Pineau, Javoy, and Allegre, 1973) whereas those of the sedimentary and metamorphic carbonates (−2.7 to −1.2) are typical of shallow-marine carbonates (Clayton and Degens, 1959; Keith and Weber, 1964; Clayton, Muffler, and White, 1968; Veizer and Hoefs, 1976). There is no apparent correlation of the $\delta^{13}C$ values of skarn calcites with distance from the intrusive contact or with skarn mineralogy (table 2).

The transition in isotopic composition of carbonate between marble and skarn appears to be very abrupt, as shown in figure 5. Isotopic analyses of calcites along a traverse across the marble/skarn interface indicate that ^{13}C- and ^{18}O-depletions are restricted to a narrow ($\leqslant$ 1 cm) zone adjacent to the skarn. This zone also corresponds to a mineralogical transition (calcite + dolomite + forsterite) between the pyroxene skarn and marble (calcite + dolomite + forsterite + periclase (brucite) + spinel). This sample is further discussed in Bowman and Essene (1984).

Oxygen isotope compositions of skarn silicates.—Skarn silicate minerals are tremendously depleted in ^{18}O relative to their marble precursors but are also slightly enriched in ^{18}O relative to the minerals from the Black Butte stock. These relations can be seen most directly in the pyroxene and amphibole data (figs. 3 and 4). The order of ^{18}O-enrichment in the skarns is: calcite > plagioclase > amphibole > mica > garnet $\cong$ pyroxene. Some skarn garnets are ^{18}O-depleted relative to pyroxene, a reversal of the 2 permil enrichment suggested by experiments and empirical calculations (Bottinga and Javoy, 1975; Taylor and O'Neil, 1977)

at 500° to 550°C, the estimated temperature range of skarn formation (Bowman and Essene, 1984). These samples may simply be out of isotopic equilibrium.

There are large $\delta^{18}O$ variations in skarn minerals within the skarns (figs. 3 and 4). For example, the $\delta^{18}O$ values of pyroxenes vary from 6.9 to 12.2 permil. The variation in $\delta^{18}O$ values of plagioclase, amphibole, and calcite are smaller, but significant nonetheless. The $\delta^{18}O$ values of skarn silicates increase, in general, with increasing distance of the sample from the igneous contact (fig. 3). This correlation also holds, albeit imperfectly, for the two areas sampled in greatest detail (area II, traverse B-B′, fig. 3). The large variation in $\delta^{18}O$ values of pyroxenes in the Elkhorn skarns contrasts with the narrow range of $\delta^{18}O$ values that characterizes pyroxenes from the Osgood Mountains, Nev. (2.3 permil variation), Pine Creek, Calif. (1.8 permil variation), and CanTung, Northwest Territories (1.0 permil variation) skarns (Taylor and O'Neil, 1977; Brown, Bowman, and Kelly, 1985; Bowman and others, 1985).

The large ^{18}O variations in the Elkhorn skarn imply either large variations in the temperature of skarn formation or significant variations in the $\delta^{18}O$ values of the skarn-forming fluids. Oxygen isotope temperatures calculated from 10 plagioclase–pyroxene and 15 calcite–pyroxene pairs, utilizing the fractionation factors of Bottinga and Javoy (1973, 1975) and O'Neil, Clayton, and Mayeda (1969), define temperatures between

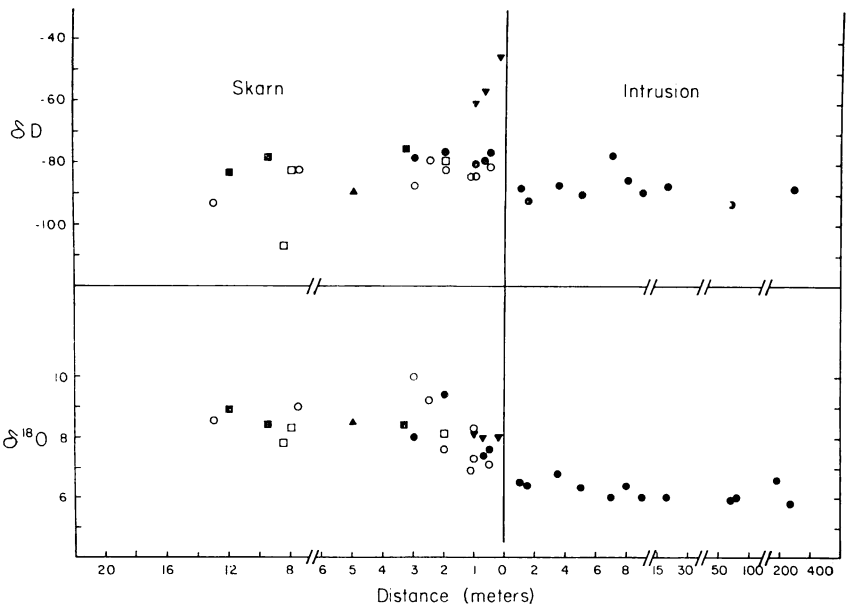


Fig. 4. Plot of the δD and $\delta^{18}O$ values of hydrous silicates from the Black Butte stock and skarns, plotted versus distance from the intrusive contact. Mineral symbols are: amphibole (circles); micas (squares); stage I epidote (inverted triangles); chlorite (triangles). Symbols for stage I skarns are solid, symbols for stage II skarns are open.

420° and 680°C. Temperatures based on the experimental data for pyroxene from Matthews, Goldsmith, and Clayton (1983) are typically 25°C lower. All but seven of the 25 temperature determinations fall within a considerably narrower range of 440° to 595°C, a range broadly consistent with temperatures of 525° ± 35°C estimated for skarn formation (Bowman and Essene, 1984). Although the range of isotopic temperatures is comparatively large, there is no systematic variation in these temperatures, either from *Cc-Px* or *Pg-Px* pairs, with distance of the sample from the igneous contact, as would be expected if the variations in $\delta^{18}O$ values of the skarn minerals were the result of temperature gradients during formation of the skarn. In addition, phase equilibrium evidence does not support the presence of significant thermal gradients in the skarns (Bowman and Essene, 1984). Further, even a temperature decrease of 150°C would produce an increase of only about 1 permil in the $\delta^{18}O$ value of the pyroxene, so clearly the bulk of the observed isotopic variation reflects variation in the $\delta^{18}O$ value of the skarn fluids. The comparatively large range of isotopic temperatures most likely results from small (for example, < 0.5 permil) departures from isotopic exchange equilibrium between minerals.

Hydrogen isotope variations.—Figure 4 is a compilation of δD and $\delta^{18}O$ values for hydrous silicates, plotted as a function of distance from the intrusive contact. The figure illustrates the systematic increase in $\delta^{18}O$ values away from the intrusive contact and the absence of any spatial correlation involving δD values of the skarn hydrous silicates.

The δD values of igneous amphiboles vary from −93 to −77 permil, skarn amphiboles and micas from −107 to −75 permil, and marble micas and amphiboles from −97 to −65 permil (tables 1, 2, and 3). The skarn

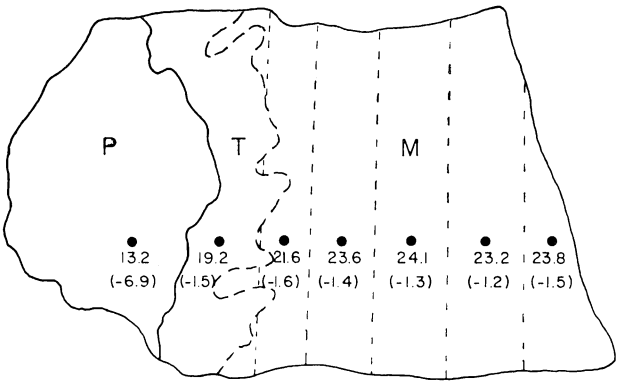


Fig. 5. Sketch of a polished slab 12 cm in long dimension (pl. 3-C in Bowman and Essene, 1984) which contains the marble/skarn interface. Abbreviations are: P = pyroxene skarn (zone E); T = transition zone without periclase; M = periclase marble. Carbon (parentheses) and oxygen isotope analyses of calcite from a traverse across the interface are also shown on the sketch. Each analysis is of a zone of approx 1 cm width, normal to the traverse; the solid circle marks the midpoint of each of these zones. The analyses indicate that ^{13}C- and ^{18}O-depletions are restricted to a narrow zone (less than 1 cm) adjacent to the skarn.

amphiboles have slightly higher D/H ratios and lower iron contents than the igneous amphiboles, indicating that the two groups have, on average, equilibrated with fluids of quite similar δD values (−59 to −55) at equivalent temperatures. The δD values of the epidotes are 18 to 20 permil enriched relative to those of coexisting amphibole. Clintonite appears to be typically enriched by 5 to 10 permil in deuterium relative to the other layer silicates and amphiboles, which indicates that substitution of aluminum in the octahedral site in micas decreases the hydrogen isotope fractionation factor between mica and water, as found in the experiments of Suzuoki and Epstein (1976). All the epidotes with δD values lower than −71 permil are late replacement or vein phases (stages III and IV), as are the D-depleted serpentine and chlorite from the shear zones (stage IV). None of the igneous or stage I and II skarn hydrous silicates has the very low δD values that are characteristic of rocks that have interacted with isotopically light meteoric water (Taylor, 1974). In contrast, the late-stage epidote veins (stage III) and shear zone replacement minerals serpentine and chlorite (stage IV) are markedly lighter, suggesting significantly different origins for the fluids that produced them.

The δD values of hydrous silicates from the marbles vary widely from −97 to −65. All these phases are essentially magnesium endmembers, so the δD variations cannot be due to variations in Fe/(Fe + Mg) ratios. Nor can the 32 permil variation be the result of the approx 100°C difference in metamorphic temperature between these two samples (E3-66 and E2-62). This variation in δD value reflects either the presence of an isotopically heterogeneous metamorphic pore fluid or lack of hydrogen isotope equilibrium.

ORIGIN OF THE SKARN CALCITE

Skarn calcite is significantly depleted in both ^{18}O and ^{13}C relative to marble calcite as shown in figure 6. These depletions are similar to those observed in several other localities where decarbonation reactions have taken place (Rye, 1966; Rye, Hall, and Ohmoto, 1974; Rumble and others, 1982; Taylor and O'Neil, 1977; Nabelek and others, 1984; Valley and O'Neil, 1984; Brown, Bowman, and Kelly, 1985). The skarn calcites have relatively homogeneous $\delta^{13}C$ values (−7.8 to −6.0 permil) that are similar to those of magmatic carbon (Taylor, Frechen, and Degens, 1967; Conway and Taylor, 1969; Deines, 1970). However, the $\delta^{18}O$ values vary comparatively widely from values in near equilibrium with the Black Butte stock to values over 3 permil higher. These isotopic data are consistent with derivation of the oxygen and carbon in the skarn calcites largely from fluids that were equilibrated isotopically with the Black Butte stock, with some contribution of oxygen from the high $\delta^{18}O$ marble wallrock.

As ^{18}O- and ^{13}C-depletions have been ascribed to decarbonation processes in skarn (Shieh and Taylor, 1969) and contact metamorphosed marbles (Lattanzi, Rye, and Rice, 1980), it is appropriate to evaluate if decarbonation processes can produce the ^{18}O- and ^{13}C-depletions observed between marble and skarn calcites at Elkhorn. The progressive depletions in ^{18}O and ^{13}C that would result from equilibrium decarbonation of the

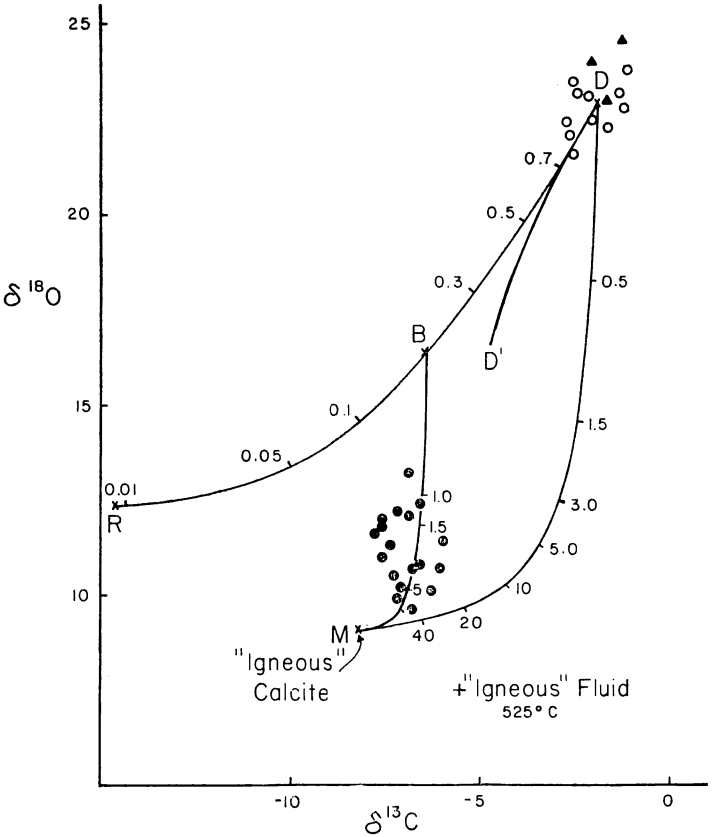


Fig. 6. Plot of $\delta^{18}O$ versus $\delta^{13}C$ values for calcites and dolomites from sedimentary dolostone (solid triangles), marble (open circles), and skarn (solid circles). The line D-D′ is the trend of ^{13}C- and ^{18}O-depletion which would result from simple single-stage decarbonation of average marble ($\delta^{18}O = 22.9$; $\delta^{13}C = -2.0$). Line D-R is an equivalent continuous removal (Rayleigh distillation) decarbonation trend. The line is marked off with the fraction of residual carbonate left. Line D-B-M is discussed in the text. The line D-M represents ^{18}O- and ^{13}C-depletions in calcite resulting from isotopic exchange between average marble and "magmatic" fluid with $\delta^{18}O = 7.5$, $X(CO_2) = 0.02$, and $\delta^{13}C = -5.5$. The line is marked with atomic oxygen ratios of "magmatic" fluid (W) to marble rock (R). Mass-balance relations used here are summarized in the appendix. Equilibrium C–O isotope fractionations of O'Neil and Epstein (1966), O'Neil, Clayton, and Mayeda (1969), and Bottinga (1969) and appropriate factors compiled in Friedman and O'Neil (1977) were used.

wallrock marble ($\delta^{18}O = 22.9$; $\delta^{13}C = -2.0$), under either single-stage or continuous (Rayleigh distillation) fluid removal at 525°C, are illustrated by the curves D-D′ and D-R in figure 6. These curves and mass-balance calculations (table 4) indicate that the $\delta^{13}C$ and $\delta^{18}O$ values of skarn calcites could not develop solely through decarbonation of the marble wallrock. Single-stage decarbonation does not produce sufficient depletion in either ^{18}O or ^{13}C (fig. 6, line D-D′). Continuous decarbonation (Ray-

leigh distillation) could produce sufficient ^{13}C-depletion but not sufficient ^{18}O-depletion (line D-R).

Decarbonation alone, even under conditions of continuous fluid removal, can produce only limited ^{18}O-depletion because not all the oxygen atoms initially present in the dolomite can be removed as CO_2; some fraction of the original oxygen remains in newly formed silicate minerals. During the conversion of dolomitic marble to a massive diopside skarn:

$$\text{Dol} + 2\,(SiO_2)_{aq} = \text{Di} + 2\,CO_2 \qquad (2)$$

one-third of the oxygen originally present in the dolomite remains in the system in diopside. If one considers oxygen from the externally derived SiO_2, or if SiO_2 in the form of quartz is originally in the rock, as would be the case for isochemical contact metamorphism, then only 40 percent of the original oxygen can be removed in CO_2. In the case of isochemical metamorphism, maximum ^{18}O depletion is even more limited (Valley and O'Neil, 1984). In the case of skarn formation, the amount of ^{18}O deple-

TABLE 4

Calculated ^{13}C- and ^{18}O-depletions resulting from simple decarbonation of average marble calcite ($\delta^{18}O = +22.9$, $\delta^{13}C = -2.0$) at 525°C under both continuous (Rayleigh distillation) and single-stage (parentheses) fluid removal conditions

Mole fraction C Remaining in Marble	Mole fraction O Remaining in Marble*	Δ O CO_2-Rock**	$\delta^{18}O$ (Resid. Ce)†	$\delta^{13}C$ (Resid. Ce)†
0.9	0.933	+6.8	+22.4 (+22.4)	-2.3 (-2.3)
0.7	0.800	+7.1	+21.3 (+21.5)	-3.0 (-2.8)
0.5	0.667	+7.4	+19.9 (+20.4)	-3.9 (-3.4)
0.3	0.533	+8.0	+18.0 (+19.2)	-5.2 (-4.0)
0.1	0.400	+9.0	+14.6 (+17.5)	-8.2 (-4.5)
0.05	0.367	+9.3	+13.4 (+17.0)	-10.0 (-4.7)
0.01	0.340	+9.6	+12.4 (+16.6)	-14.3 (-4.8)

* The fraction of residual oxygen remaining after actual decarbonation reactions is not zero, but 0.33 or greater, as illustrated by the skarn front reaction Dol + 2 $(SiO_2)_{aq}$ = Di + 2 CO_2. Four out of the original six oxygens in the dolomite have been removed in CO_2 gas. Actual reaction also involved addition of oxygen (4 moles/mole dolomite) in the form $(SiO_2)_{aq}$ by the metasomatic fluid, which is ignored in these calculations.

** This fractionation factor is not constant because of the changing proportions of dolomite and diopside (see *) accompanying progressive decarbonation. The factors were calculated at 0.1 intervals of the residual mass fraction (0.05 below 0.1 residual carbon) using the proportions of dolomite to diopside computed from the previous step and using the fractionation factors of O'Neil and Epstein (1966) and Bottinga and Javoy (1975).

† The ^{18}O- and ^{13}C-depletions were calculated under single-stage (parentheses) and continuous (Rayleigh distillation) fluid removal conditions.

tion depends primarily on the fluid/rock ratio and the $\delta^{18}O$ value of the skarn fluid, which in turn is defined largely by the $\delta^{18}O$ value of the adjacent pluton. The oxygen isotope effects of decarbonation are of secondary importance.

The $\delta^{13}C$-$\delta^{18}O$ trend (line D-M) that would result from progressive interaction between igneous fluids ($\delta^{13}C = -5.5$, $X(CO_2) = 0.02$, $\delta^{18}O = 7.5$) and the wallrock carbonate ($\delta^{13}C = -2.0$, $\delta^{18}O = 22.9$) is shown in figure 6. Point M represents the $\delta^{18}O$ and $\delta^{13}C$ values of calcite in equilibrium with the igneous fluid endmember at 525°C. The lowest $\delta^{18}O$ values of the skarn calcites can be accounted for by such fluid-rock interaction at very high fluid/rock (W/R) ratios of > 30. The array of higher $\delta^{18}O$ values could result either from lower temperatures of formation (< 525°C) or a combination of variable but limited decarbonation and extensive interaction with 1 to 8 times the mass of oxygen in magmatic fluid (such as line D-B-M, fig. 6). Very large temperature decreases ($\sim$ 195°C) from the igneous contact to the skarn/marble boundary would be required to produce the observed increase of 3.3 permil in the $\delta^{18}O$ values of the skarn calcites. Such large thermal gradients in the skarn are not supported by either phase equilibrium evidence (Bowman and Essene, 1984) or oxygen isotope geothermometry results (see above).

Potential interactions between the skarn fluid and low-^{13}C organic material or graphite in the carbonate wallrocks or formation of significant amounts of CH_4 in the skarn fluids could influence the $\delta^{13}C$ values of the skarn calcites. However, such effects are unlikely because graphite is absent from both skarn and wallrocks. In addition, CH_4 is present at quantitatively negligible levels (< 0.05 mol fraction) at the P-T-f(O_2) conditions of early skarn formation (Bowman and Essene, 1984).

ORIGIN OF SKARN FLUIDS

The temperature of stage I skarn formation was estimated at 525° ± 35°C based on phase equilibria considerations (Bowman and Essene, 1984). Oxygen isotope temperatures are consistent with this estimate. We have calculated the hydrogen and oxygen isotope composition of fluids in equilibrium with the Black Butte intrusion, stage I skarns, and host marble at 525°C, using the mineral fractionation factors summarized above and in Friedman and O'Neil (1977) (fig. 7). The range of possible δD and $\delta^{18}O$ values of water in exchange equilibrium with the Black Butte stock over the temperature range 500° to 650°C is illustrated in figure 7 by the box labeled magmatic water. Phase equilibrium studies (Bowman, ms; Bowman and Essene, 1984) limit the formation of stage II skarn to temperatures below 475° to 525°C. The hydrogen and oxygen isotope compositions of the stage II fluids plotted in figure 7 were calculated at 525°C, the maximum likely temperature of their formation. The effect of formation at lower temperature (for example, 475°C) is illustrated by the bar attached to one of the samples. Calculations using minimum likely temperature for the igneous component (for example, 525°C) and maximum likely temperatures for skarn stages I and II produce the maximum differences in δD and $\delta^{18}O$ values between the skarn

fluids and fluid in equilibrium with the Black Butte stock. The result is a maximum estimate of the amount of meteoric water in the skarn fluids. The calculation of maximum likely $\delta^{18}O$ values for skarn fluids also provides a maximum estimate of the extent of interaction with the high ^{18}O wallrock. Temperatures of 425° and 350°C were assumed for stages III and IV, respectively (Bowman, ms).

The means of the calculated δD values for both stage I skarn fluids (−59) and, with two exceptions, stage II fluids (−62), are almost identical to each other and very similar to that of fluid in equilibrium with the Black Butte quartz diorite (−55). However, these fluids are dramatically

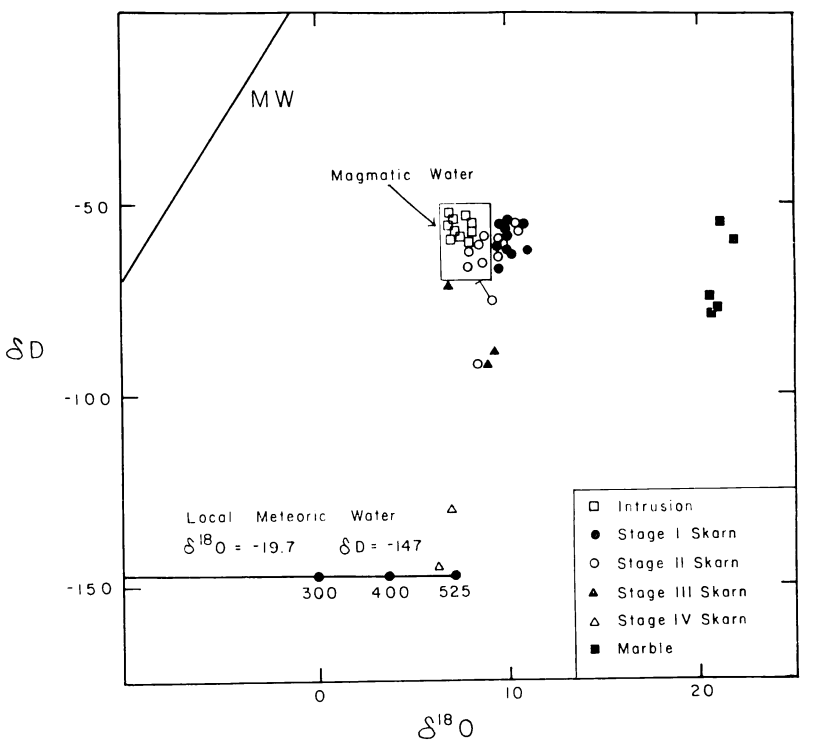


Fig. 7. Plot of δD and $\delta^{18}O$ values of fluids in isotopic equilibrium with the Black Butte stock, stages I through IV skarns, and marble at 525°C. Symbols are: intrusion (open squares); marble (solid squares); stage I skarn (solid circles); stage II skarn (open circles); stage III skarn (solid triangles); stage IV skarns (open triangles). Only those samples for which both δD and $\delta^{18}O$ values could be analyzed are plotted. Thus the full range of $\delta^{18}O$ values from the stage I skarn fluids is not reflected in this figure. The δD and $\delta^{18}O$ values of stages III and IV were calculated at 425° and 350°C, respectively. The oxygen isotope compositions of heated meteoric waters in isotope exchange equilibrium with igneous rock ($\delta^{18}O$ = 7.0 permil) at 300°, 400°, and 525°C are also included, as is the meteoric water line (MW) for reference (Craig, 1961a). Calculated δD values are based on the experimental data of Suzuoki and Epstein (1976). Calculated $\delta^{18}O$ values are based on the feldspar fractionation data of O'Neil and Taylor (1967), quartz fractionation data of Bottinga and Javoy (1973, 1975), the calcite fractionation data of O'Neil, Clayton, and Mayeda (1969), and the fractionation factors for *Pg-Px* and *Pg-Amp* pairs which were empirically derived by Bottinga and Javoy (1975).

heavier than present-day meteoric water in the area (−147). The calculated $\delta^{18}O$ value of stage I fluid varies from 7.9 nearest the intrusive contact to 13.2 permil near the skarn-marble interface. The $\delta^{18}O$ values of skarn fluids nearest the intrusion are isotopically very similar to fluids in equilibrium with the Black Butte quartz diorite (7.5) but are dramatically higher than those of local meteoric water (−19.7). The hydrogen and oxygen isotope compositions of skarn fluids indicate that little or no meteoric water was involved in either stage I or II of skarn formation at Elkhorn. Based on a δD value of −147 for present-day meteoric water in the area, meteoric water would comprise only about 8 mol percent or less of the stage I and II skarn fluids.

The presence of significantly lower δD values for stage III and stage IV skarn fluids can be accounted for most simply by progressive increases in the component of isotopically light meteoric water. Stage III vein fluids could have involved up to 30 to 45 percent meteoric water, whereas stage IV (serpentine/chlorite) fluids were certainly dominated by meteoric water.

TABLE 5

Oxygen isotope effects of exchange between formation water ($\delta^{18}O_i = 7.0$) and marble ($\delta^{18}O_i = 22.9$) or igneous rock ($\delta^{18}O_i = 8.0$)*

	Marble-H_2O Exchange**		Intrusion-H_2O Exchange†	
W/R (% O)	δ^f_W	δ^f_R	δ^f_W	δ^f_R
0.01	21.3	22.8	7.3	8.1
0.1	20.1	21.6	8.5	9.3
0.2	19.0	20.5	9.6	10.4
0.3	18.1	19.6	10.5	11.3
0.5	16.6	18.1	11.9	12.7
1.0	14.2	15.7	14.3	15.1
1.5	12.8	14.3	15.7	16.5
2.0	11.8	13.3	16.6	17.5

* The dolomite–H_2O and plagioclase (An_{30})–H_2O fractionation factors used for these calculations are from O'Neil, Clayton, and Mayeda (1969) and O'Neil and Taylor (1967).

** The left side of this plot illustrates the ^{18}O-enrichment in formation water that would result from progressive isotope exchange at 525°C with the marble of the Black Butte aureole.

† The right side of the plot summarizes the progressive ^{18}O-enrichment of the Black Butte stock and accompanying ^{18}O-depletion in formation water ($\delta^{18}O = +18.5$, initially equilibrated with the marble) which would result from their progressive interaction.

The lowest calculated δD values (−132 and −145) of the stage IV fluids may be taken as an estimate of the δD value of meteoric water in the Elkhorn area during skarn formation in the Late Cretaceous (90-92 Ma). Because these stage IV fluids may contain some component of magmatic or other high-δD fluid, these values represent upper limits to the estimate. If the stage III and IV minerals formed at significantly lower temperatures than estimated here, our estimate would be too low. However, fractionation factors for most hydrous silicates do not increase significantly below 350°C, and in fact some may decrease (for example, Sakai and Tsutsumi, 1978; Lambert and Epstein, 1980). Hence, our estimate for the δD values of stages III and IV fluids is probably not sensitive to the temperature estimated for skarn formation. Based on this evidence, meteoric water during Late Cretaceous in the Elkhorn area was no more than 15 permil heavier than present-day meteoric water in the area. If a δD value as heavy as −132 is taken for meteoric water, then the average amount of meteoric water in the stage I and II fluids would be at most 10 mol percent.

The close similarity in hydrogen and oxygen isotopic composition between stages I and II skarn fluids and igneous fluids is consistent with derivation of fluids for both stages by equilibration with isotopically normal igneous rock. The most obvious origin of such fluids is magmatic water exsolved during crystallization of the quartz diorite. However, the δD values of magmatic fluid and certain formation waters (Hitchon and Friedman, 1969) are similar, so derivation of the skarn-forming fluids from the latter fluid type cannot be ruled out completely from the hydrogen-isotope data alone.

Geological, petrological, and oxygen-isotope data provide independent evidence that, whatever the initial origin of the skarn-forming fluids, these fluids *last* equilibrated with the Black Butte stock or a deeper equivalent. The concentration of skarn development on the top and upper sides of the Black Butte stock dictates that the skarn fluids ascended near-vertically through the stock and stock margins to reach these sites of skarn development. The presence of wallrocks dominated by high-$\delta^{18}O$ carbonates further dictates that any heated (~ 525°C) formation water generated within the carbonates, or that flowed through the carbonates, would have high $\delta^{18}O$ values (18 to 19) unsuitable to form skarn directly. These fluids would also be chemically incompatible with skarn mineralogy. The presence of abundant garnet + pyroxene + sphene assemblages in the skarns restricts log $a(SiO_2)$ values to greater than −1.65 (fig. 9 in Bowman and Essene, 1984). In contrast, fluids equilibrated with the periclase + forsterite-bearing marbles of the Black Butte stock aureole would have log $a(SiO_2)$ values of −4.0 or less. These ^{18}O-enriched, low $a(SiO_2)$ fluids would first have to exchange chemically and isotopically with large amounts of the Black Butte stock before participating in skarn formation. In order to be compatible with the limited ^{18}O-enrichment (< 1.0 permil in all but one sample) measured in the stock margin (zones from 1-8 m thick) and to produce fluids with $\delta^{18}O$ values sufficiently low

($\leqslant$ 8 permil) to form the inner skarns, this fluid-rock exchange would have occurred at formation water (W): igneous rock (R) atomic oxygen ratios of less than 0.10 to 0.15 (table 5). Alternatively, for a formation water to retain a $\delta^{18}O$ value sufficiently low to produce the inner skarns directly, interaction with the marble would have to take place at very high W/R (marble) ratios (atomic oxygen). However, the large zones of significant ^{18}O-depletion in marble near the intrusive contact which would result under such conditions have not been detected in the marble at the present level of exposure.

INTERACTION OF SKARN FLUIDS WITH CARBONATE WALLROCK

The calculated hydrogen isotope compositions of the early skarn fluids are in virtual exchange equilibrium with the Black Butte stock, but the $\delta^{18}O$ values of the Massive skarns vary considerably with a systematic increase in ^{18}O outward from the igneous contact. The $\delta^{18}O$ values range from those in equilibrium with the Black Butte stock to values as much as 5 permil higher (fig. 3). This ^{18}O-enrichment must be the result either of an outward decline in temperature of skarn formation or of progressive isotopic exchange with the high $\delta^{18}O$ carbonate wallrock. Possible variations in temperature cannot cause this much ^{18}O-enrichment, however. Even a temperature drop of 150°C would produce only about 1 permil increase in the $\delta^{18}O$ values of the skarn pyroxenes. The maximum possible variation in the temperature of skarn formation is about 100°C and is likely considerably less (Bowman and Essene, 1984). Further, there is no petrological (Bowman and Essene, 1984) or isotopic evidence for significant (for example, $>$ 50°C) thermal gradients in the skarns. Therefore, the systematic increase in $\delta^{18}O$ values of the skarn fluids during outward growth of the zoned skarns is probably the result of interaction with the high-^{18}O marble wallrock.

Oxygen isotope exchange between the skarn fluids and the high-$\delta^{18}O$ carbonate wallrock could take the form either of exchange between the skarn fluids and wallrock or, as suggested by Taylor and O'Neil (1977), mixing of the H_2O-rich skarn fluid with ^{18}O-enriched CO_2 evolved from the marble during its reaction to skarn. Isotopic exchange involving the enclosed metamorphic pore fluids is not likely to be significant, as these fluids do not constitute a quantitatively important source of oxygen in the wallrocks. Regardless, ^{18}O-exchange involving these fluids will be nearly equivalent to exchange with the carbonate rock itself.

Given the average measured $\delta^{18}O$ values of the marbles (23) and the $\delta^{18}O$ values of fluid in equilibrium with the Black Butte stock (8.0 $\pm$ 0.5), the minimum skarn fluid (W_s) to bulk marble (R_m) atomic oxygen ratios required to produce the observed $\delta^{18}O$ values of the skarns can be computed. The minimum W_s/R_m ratios required to produce the observed changes in the $\delta^{18}O$ values of skarn pyroxenes vary from 1.4 at the marble-skarn interface to $>$ 40 at the intrusive contact (table 6 and fig. 8). Depending on the initial composition chosen for the skarn fluid, the average W/R ratio would vary from 5 to 9. Clearly, large masses of

skarn fluid, relative to the mass of marble replaced, were involved in the skarn formation at Elkhorn.

The progressive ^{18}O-enrichments also could have been produced by progressive mixing of H_2O-rich skarn fluids with CO_2 evolved during transformation of marble to skarn, as suggested by Taylor and O'Neil (1977). Mass-transfer calculations for conversion of marble to massive garnet–pyroxene or pyroxene skarn at any reasonable volume change require the evolution of substantial amounts of CO_2 (Bowman, ms). This CO_2 would be expected to migrate down chemical potential and/or density gradients into the developing skarn, progressively mixing with the initial H_2O-rich skarn fluids. This CO_2 is also likely to exchange isotopically with incoming H_2O-rich skarn fluids, producing a positive correlation between $\delta^{18}O$ values of skarn minerals and increasing $X(CO_2)$ in the mixed skarn fluids (Taylor and O'Neil, 1977).

The ^{18}O effects resulting from progressive mixing of H_2O equilibrated with the Black Butte intrusion ($\delta^{18}O = 8.0 \pm 0.5$) with CO_2 evolved from the host marble ($\delta^{18}O = 30$) are compiled in table 7 and illustrated in figure 9. Details of these calculations are presented in the appendix. Given the endmember values stated above, the mol fraction of CO_2 required to

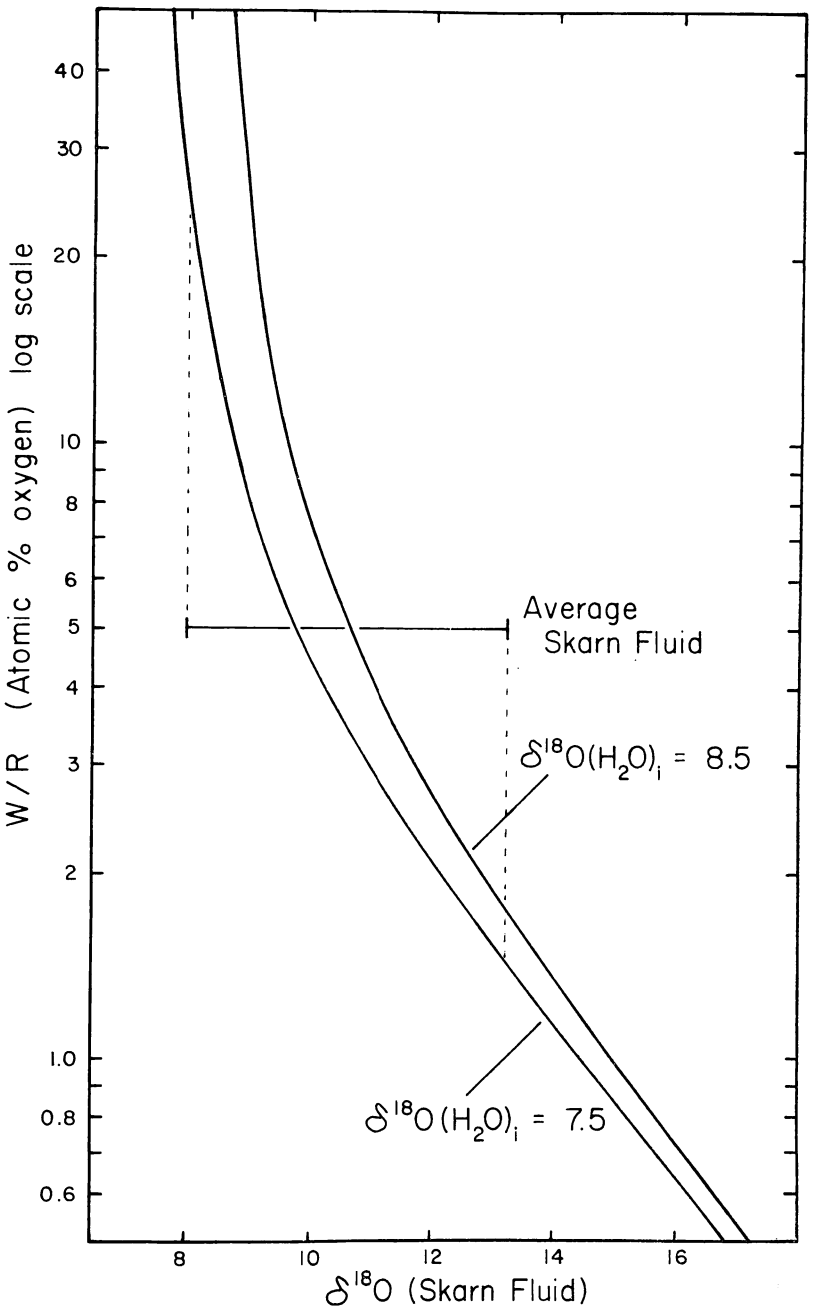
TABLE 6

Oxygen isotope effects of progressive interaction between H_2O-rich skarn fluid and marble wallrock ($\delta^{18}O_i = 22.9$)*

W/R (atom % oxygen)	Final δ^{18}O (skarn calcite)**		
	$\delta^{18}O(H_2O)_i = 7.5$		$\delta^{18}O(H_2O)_i = 8.5$
0.1	21.6		21.8
0.25	20.1		20.4
0.5	18.3		18.7
1.0	16.0		16.5
2.0	13.6		14.3
3.0	12.5		13.2
5.0	11.3		12.2
6.0	11.0	Equilibrium	11.8
7.0	10.7	with	11.6
8.0	10.5	skarn pyroxene	11.4
10.0	10.3		11.2
15.0	9.9		10.8
20.0	9.7		10.6
30.0	9.4		10.4
40.0	9.3		10.3

* Fractionation data used in these calculations are from O'Neil, Clayton, and Mayeda (1969). Calculation procedures are summarized in the Appendix.

** The bars indicate the range of $\delta^{18}O$ values of calcite in equilibrium with skarn pyroxene at 525°C.


40
30
20
10
8
6
5
4
3
2
1.0
0.8
0.6
W / R (Atomic % oxygen) log scale
Average
Skarn Fluid
$\delta^{18}O(H_2O)_i$ = 8.5
$\delta^{18}O(H_2O)_i$ = 7.5
8
10
12
14
16
$\delta^{18}O$ (Skarn Fluid)

produce the ^{18}O-enrichment in the skarn fluids would vary from as low as 0.00 at the intrusive contact to 0.25 at the marble/skarn interface. All but two of the measured $\delta^{18}O$ values from the skarns require $X(CO_2)$ values of 0.19 or less. Application of experimental and calculated phase equilibria to observed skarn assemblages at Elkhorn restricts $X(CO_2)$ to between 0.03 and 0.30 during stage I skarn formation (Bowman and Essene, 1984). The reasonable agreement of these petrologically defined limits of $X(CO_2)$ with those calculated from the oxygen isotope H_2O/CO_2 mixing model provides support for both the H_2O–CO_2 mixing process and the initial $\delta^{18}O$ values assumed for the two endmember components.

In their calculations of $X(CO_2)$ limits based on oxygen isotope data from the Osgood Mountains, Nev., Taylor and O'Neil (1977) concluded that the fluids that formed massive skarn were very water-rich, < 0.04 $X(CO_2)$. Although water-rich skarn fluids are indicated at both Osgood Mountains and Elkhorn by the oxygen isotope data, both the upper limit and the variability of $X(CO_2)$ values at Elkhorn are greater.

Petrologic constraints to skarn fluid/wallrock interaction.—If H_2O/CO_2 mixing produced both the mineral zonation and the $\delta^{18}O$ variations in the Elkhorn skarns, then limits to $X(CO_2)$ values for individual skarn zones, calculated from the oxygen isotope data, should also be consistent with limits defined by skarn mineralogy. A comparison of petrologically and isotopically defined limits to $X(CO_2)$ for the skarn zones is provided in table 8. The petrologically defined limits to $X(CO_2)$ and the phase equilibria used to define these limits are discussed in detail in Bowman and Essene (1984). The $X(CO_2)$ limits defined by the phase equilibria discussed below have been adjusted for the effects of typical solid solutions in the skarn minerals, as discussed in Bowman and Essene (1984). There is a surprisingly good correspondence between the ranges in $X(CO_2)$ inferred for individual mineral assemblages by the two independent methods. The $X(CO_2)$ range of 0.02 to 0.14 defined by $\delta^{18}O$ values for garnet-bearing assemblages (zones A-D) is consistent with, but more restrictive than, the limits of 0.00 to 0.22 defined at 525°C by the reaction (Gordon and Greenwood, 1971; Kerrick, 1974):

$$An + 2\,Cc + Qz = Gr + 2\,CO_2 \qquad (3)$$

The assemblage garnet + plagioclase + pyroxene + calcite (zone D) is restricted at 525°C to $0.05 < X(CO_2) < 0.22$ by reaction 3 and the reaction (Johannes and Orville, 1972; Kerrick, 1974):

$$2\,Zo + CO_2 = 3\,An + Cc + H_2O \qquad (4)$$

← Fig. 8. Plot of $\delta^{18}O$ values of skarn fluid versus the atomic oxygen ratio of initial skarn fluid (W) to marble wallrock (R) (log-scale). The initial $\delta^{18}O$ value of the marble wallrock is 22.9 permil. Initial $\delta^{18}O$ values of skarn fluids (7.5, 8.5 permil) are those in equilibrium with the range of observed $\delta^{18}O$ values of the Black Butte stock at 525°C. The horizontal bar indicates the range of calculated $\delta^{18}O$ values of fluids in equilibrium with skarn pyroxenes (6.9 to 12.2 permil). The bar is plotted at an average minimum W/R ratio of 5, which would be defined using an initial and average $\delta^{18}O$ value for the skarn fluid of 7.5 and 9.7 permil, respectively.

Oxygen isotope limits for this assemblage are a more restrictive $0.03 < X(CO_2) < 0.09$. There is good agreement between the two sets of data for epidote-bearing assemblages of zone A (compare the range of 0.00 to 0.11 to oxygen isotope limits of 0.00 to 0.10). However, there is only a partial overlap of $X(CO_2)$ limits for the several garnet-absent assemblages of zone E (table 8).

In general, the upper limits to $X(CO_2)$ are significantly more restricted by the isotope mixing model than by the phase equilibria data. Such discrepancies are not surprising, given the possibility that additional variables — $a(SiO_2)$, for example — may also produce mineral zonation in the Elkhorn skarns (Bowman and Essene, 1984). Additionally, it is possible that the $\delta^{18}O$ values of fluids could depend on other factors such as variations in initial $\delta^{18}O$ of skarn fluids through space and time. Discrepancies involving clintonite (*Clt*)- and vesuvianite (*Vs*)-bearing assemblages could also result from errors in our preliminary placement of reaction equilibria involving these phases (Bowman and Essene, 1979). Another potentially significant factor is the effect of dissolved NaCl on the T-$X(CO_2)$ locations of appropriate phase equilibria (Bowers and Helgeson, 1983a, b).

TABLE 7

Oxygen-isotope effects of progressive mixing, at 525°C, of initial skarn H_2O ($\delta^{18}O = 7.5$ or 8.5) with CO_2 ($\delta^{18}O = 30$) evolved during transformation of marble to skarn

$X_O^{CO_2}$	X_{CO_2}	$\delta^{18}O$ H_2O (f)*	$\delta^{18}O$ CO_2 (f)*	$\delta^{18}O$ system (H_2O + CO_2)*
0.095	0.05	8.8 (9.7)	17.6 (18.5)	9.6 (10.5)
0.182	0.10	10.0 (10.8)	18.8 (19.6)	11.6 (12.4)
0.261	0.15	11.1 (11.8)	19.9 (20.6)	13.4 (14.1)
0.333	0.20	12.0 (12.7)	20.8 (21.5)	15.0 (15.7)
0.400	0.25	13.0 (13.6)	21.8 (22.4)	16.5 (17.1)
0.462	0.30	13.8 (14.4)	22.7 (23.2)	17.9 (18.4)
0.518	0.35	14.6 (15.1)	23.4 (23.9)	19.2 (19.6)
0.571	0.40	15.3 (15.8)	24.1 (24.5)	20.4 (20.8)
0.667	0.50	16.6 (16.9)	25.4 (25.8)	22.5 (22.8)
0.750	0.60	17.7 (18.0)	26.6 (26.8)	24.4 (24.6)
0.824	0.70	18.7 (18.9)	27.6 (27.8)	26.0 (26.2)
0.889	0.80	19.6 (19.7)	28.5 (28.6)	27.5 (27.6)
0.947	0.90	20.4 (20.4)	29.3 (29.3)	28.8 (28.9)
0.974	0.95	20.8 (20.8)	29.6 (29.7)	29.4 (29.4)

* Delta values without parentheses were calculated with $\delta^{18}O(H_2O)_i = 7.5$ per mil; values in parentheses were calculated with $\delta^{18}O(H_2O)_i = 8.5$ per mil.

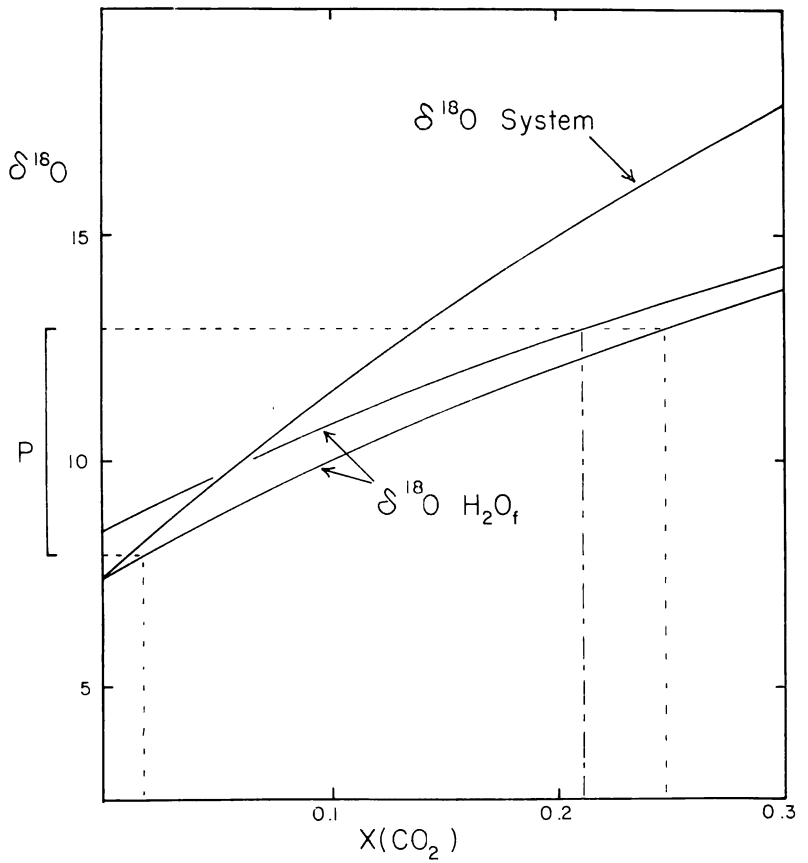


Fig. 9. Plot depicting the variation in $\delta^{18}O$ value of skarn fluid resulting from progressive mixing of initial skarn water ($\delta^{18}O_i$ = 7.5 or 8.5) and metamorphic CO_2 ($\delta^{18}O$ = 30) at 525°C. Metamorphic CO_2 is that CO_2 evolved during reaction of marble to skarn. Calculation procedures are summarized in the appendix, and results compiled in table 7. The two lower lines in the figure represent the final $\delta^{18}O$ value of water in the H_2O–CO_2 mixture after isotopic exchange. The upper line denotes the $\delta^{18}O$ value for the mixture. These $\delta^{18}O$ values are based on the fractionation factors of O'Neil and Epstein (1966) and O'Neil, Clayton, and Mayeda (1969). The $\delta^{18}O$ values of water in equilibrium with measured skarn pyroxenes (denoted by P) would require $X(CO_2)$ values between 0.0 and 0.25. This range is consistent with $X(CO_2)$ limits defined by mineral assemblages.

The typical high variance of the skarn assemblages usually precludes definition of the specific variable(s) responsible for any mineralogical change. As emphasized in part I (Bowman and Essene, 1984), few of the zone boundaries can be attributed clearly to variations in $X(CO_2)$ because additional compositional variables [$a(FeO_x)$, $f(O_2)$, $a(SiO_2)$] can produce mineralogical variations as well. These additional variables can cause shifts in the T-$X(CO_2)$ locations of otherwise definitive equilibria and thus of the petrologically defined $X(CO_2)$ limits for skarn mineral assemblages. Available evidence (Bowman and Essene, 1984) suggests that variations in these compositional variables have indeed affected the

mineralogy locally and played a part in zone-boundary reactions. For example, fluctuations in zone thicknesses and variations in the distance of any particular zone from the igneous contact may indicate that compositional variables other than $X(CO_2)$ (especially the activities of SiO_2, FeO_x, and Al_2O_3) have locally extended or restricted the stability of a particular assemblage. Variable $a(SiO_2)$ may explain in part why isotopically defined upper limits of $X(CO_2)$ for garnet-bearing assemblages are significantly lower than the petrologically defined limits. Reduction of $a(SiO_2)$ shifts the equilibrium used to define the upper limit to $X(CO_2)$ for garnet-bearing zones — reaction 3 — to higher temperature and lower $X(CO_2)$. Common garnet + pyroxene + sphene assemblages permit log $a(SiO_2)$ values as low as −1.6, which would reduce maximum $X(CO_2)$ limits by as much as 0.05, removing much of the discrepancy with the isotopically defined limits. Despite local complications, the overall effect of these additional compositional variables apparently was not sufficient to disrupt the basic consistency between petrologically and isotopically defined $X(CO_2)$ limits for skarn zones.

The petrologically defined limits to $X(CO_2)$ (table 8) are based on phase equilibria in binary H_2O–CO_2 fluids. The effect of dissolved NaCl found in skarn fluids is to increase $a(CO_2)$ and shift equilibria such as reactions 3 and 4 to higher T and lower $X(CO_2)$ values (Takenouchi and Kennedy, 1965; Jacobs and Kerrick, 1981; Bowers and Helgeson, 1983a, b). Bowman and Essene (1984) noted that the *relative* positions of equilibria

TABLE 8

Comparison of petrologically and isotopically defined limits to $X(CO_2)$ for the Massive skarn zones

Zone	Mineralogy	Limits to $X(CO_2)$ Defined by Phase Equilibrium* (at 525°C)	Limits to $X(CO_2)$ Defined by Oxygen-Isotope Data
A	Px+Ep+Sc+Cc	0.02 to 0.11	0.00 to 0.10
A	Gn + Ep ± Px ± Cc	less than 0.11	0.03 to 0.10
B	Gn+Px+Vs+Cc	less than 0.08 (approximate)	0.06 to 0.14
C	Gn+Px+Cc	0.02 to 0.22	0.02 to 0.12
D	Gn+Px+Pg±Cc	0.05 to 0.22	0.03 to 0.09
D	Gn+Px+Sp±Clt±Cc	0.05 to 0.22	0.09 to 0.11
E	Px+Sp+Cc	0.15 (approximate) to 0.40	0.07 to 0.19
E	Px+Pg	0.15 (approximate) to 0.40	0.03 to 0.25

* Petrologic limits are based on the phase equilibria data of Boettcher (1970), Bowman and Essene (1979), Gordon and Greenwood (1971), Greenwood (1967), Johannes and Orville (1972), Kerrick (1974), Liou (1973, 1974), and Newton (1966) and are discussed in Part I (Bowman and Essene, 1984).

in T-X(CO_2) section will be qualitatively unaffected but estimated that the effect of NaCl in the skarn fluids at Elkhorn would be to shift all the petrologically defined X(CO_2) limits downward, by perhaps as much as 15 to 40 percent. Such shifts would produce surprisingly close agreement with isotopically defined X(CO_2) limits in some cases (for example, zone C).

The physical-chemical environment of formation probably varied from skarn to skarn, and this may explain discrepancies between X(CO_2) values inferred from oxygen isotope measurements of mineralogically equivalent samples from separate skarn masses. This type of complication is evident in the data from vesuvianite-bearing skarns (zone B). Samples X1-6 and X2-13 are from the south skarns which appear to have been formed beneath an inward-dipping intrusive contact (fig. 1). The $\delta^{18}O$ values of pyroxene from these two samples (9.0 and 9.8) are much higher than those of pyroxene from vesuvianite-bearing samples of the east skarns (6.9-8.6). Inasmuch as the oxygen isotope trend is defined principally by samples from the east skarns (fig. 2, areas I and II), which exhibit more extensive mineralogical variation, samples X1-6 and X2-13 obviously do not fit the trend well. These higher $\delta^{18}O$ values imply increased interaction with high-^{18}O carbonate rock in the south skarns, perhaps because of lower W/R ratio or higher X(CO_2), within the limits defined by the stability of *Vs* + *Clt* assemblages.

Considering other potential variables such as possible variation in $\delta^{18}O$ values of initial skarn fluids, bulk composition, mass ratio of skarn fluid to host rock, temperature, permeability, fluid flow rates, et cetera, it is perhaps surprising that any correlation between $\delta^{18}O$ values and petrologically defined values of X(CO_2) exist at all. The $\delta^{18}O$-X(CO_2) correlation and the consistency between X(CO_2) limits — both for overall skarn and specific skarn assemblages — estimated independently by petrologic and isotopic techniques lend strong support to H_2O–CO_2 mixing as an important mechanism in determining skarn zonation in the Elkhorn skarns.

AMOUNTS OF WATER INVOLVED IN SKARN FORMATION

As discussed earlier, large minimum atomic oxygen ratios of skarn fluid to replaced marble wallrock in excess of five appear to be required to explain the average $\delta^{18}O$ values of skarn pyroxenes and calcites (table 6, fig. 8). If 8.0 permil is selected for the average $\delta^{18}O$ value of the initial skarn fluid, W/R ratios of about eight would be required. Estimates of the minimum mass of fluid involved in skarn formation at Elkhorn can be made based on these W/R ratios and on estimates of the mass of skarn in the Black Butte aureole. We have estimated the present mass of skarn exposed in the contact aureole (directly associated with the Black Butte stock) to be on the order of 1.5×10^{13} g (Bowman, ms). This estimate was calculated assuming an average skarn thickness of 5 m on the sides of the stock for a vertical distance of 80 m. The amount of skarn on or near the top of the intrusion was estimated to be 5 m in vertical thickness on average and to cover 15 percent of the present surface

area (fig. 2). For these and subsequent calculations, the Black Butte stock was highly idealized to the geometry of a vertical cylinder with a diameter of 1200 m. The mass estimates are certainly approximations because of the irregular skarn and stock geometry, discontinuous occurrences of skarns, and imperfect exposure. The values are also minima in the sense that an undetermined amount of skarn has been eroded from the top and higher apophyses of the intrusion.

Keeping in mind these idealizations, a minimum of 3.6×10^{13} to 6.5×10^{13} g of water would be required to form the Black Butte skarns, and between 1.8×10^{15} and 3.2×10^{15} g of the Black Butte intrusion would be required to produce this much skarn fluid, assuming a water content of 2 percent in the quartz diorite magma (Burnham and Davis, 1971, 1974). Different water contents will modify the required mass of intrusive rock accordingly. Assuming a geometry for the stock of a vertical cylinder with a diameter of 1200 m, these mass-balance calculations would require participation of igneous rock to a depth of at least 550 to 1000 m to generate the skarn fluid. Minimum masses of igneous rock significantly greater than that presently exposed at Elkhorn must be involved in generating the needed masses of skarn fluid.

An estimate of the minimum mass of the Black Butte stock needed for oxygen-isotope exchange with formation waters, equilibrated initially with the wallrock marble, can be made in a similar manner. Assuming isotopic exchange with the entire stock of the same dimensions as in the previous calculation, a vertical section of at least 225 to 400 m would be required to deplete the formation water to $\delta^{18}O$ values consistent with the inner skarn fluids ($\leqslant +8.0$ permil) and simultaneously keep ^{18}O-enrichments within the intrusion as a whole (excluding the outermost 8 m) to less than 1 permil, the maximum enrichment observed. This range of depths greatly exceeds the maximum vertical exposure of the Black Butte stock at Elkhorn (120 m). If isotopic exchange were to be restricted to the outermost 8 m of the stock with a maximum ^{18}O-enrichment of 1.5 permil (max W/R ratio of 0.15), as is more likely, a vertical section in excess of 550 to 1100 m would be required.

CONCLUSIONS

Formation of zoned contact skarns in the Black Butte stock aureole produced significant depletions in both ^{13}C and ^{18}O in skarn relative to host marble calcite. These depletions do not match those calculated from either single-stage or continuous (Rayleigh distillation) decarbonation of preexisting marble, which indicates that skarn calcites could not have been derived solely through decarbonation of wallrock. Additional mass-balance calculations indicate that the $\delta^{13}C$ and $\delta^{18}O$ values of the skarn calcites could have been produced by a combination of limited decarbonation and interaction with large but variable amounts of "magmatic" fluid ($\delta^{18}O = 7.5$, $\delta^{13}C = -5.5$).

The close similarity in hydrogen and oxygen isotope composition of fluids that were in equilibrium with the Black Butte stock and the stages

I and II skarns suggests that magmatic fluids (or fluids equilibrated with large masses of isotopically normal igneous rock) constitute the dominant component of early skarn fluids at Elkhorn. The isotopic data indicate that little meteoric water ($\leqslant$ 10 mol percent) was involved in skarn formation until after the initial hydration stages of skarn paragenesis (stage II). Similarly, meteoric water was not involved extensively in the formation of amphibole and biotite skarn in the CanTung, Northwest Territories scheelite skarns (Bowman and others, 1985). However, progressive influxes of meteoric water did accompany later vein (stage III) and hydration (stage IV) stages at Elkhorn. Meteoric water likely constituted up to 45 mol percent of stage III fluids and dominated stage IV fluids, if $T = 350 \pm 50°C$. The restricted entry of significant amounts of meteoric water until after the high temperature ($> 400°C$) hydration reactions at Elkhorn (stage II) contrasts with the earlier and more significant influxes of meteoric water in the skarns at the Osgood Mountains (Taylor and O'Neil, 1977), Pine Creek (Brown, Bowman, and Kelly, 1985), and Alta, Utah (Kemp and Bowman, 1984).

The hydrogen isotope data do not completely rule out the derivation of the skarn fluids from certain formation waters that are isotopically similar to magmatic water. Available geologic and isotopic evidence does suggest that direct participation of formation water derived from marble in the aureole, without prior exchange with large masses of isotopically normal igneous rocks, is unlikely. The ultimate origin of these fluids, whether evolved directly from crystallizing magma or derived from formation water hydrothermally convected through large masses of hot but crystallized igneous rock, is not completely resolved by the stable isotope data.

The oxygen isotope compositions of the stock, skarns, and wallrock marble indicate that *minimum* W/R ratios from 1.4 to > 40, averaging 5 to 9, were required to produce the measured range of $\delta^{18}O$ values of the Elkhorn skarns. Relative to the mass of marble replaced, large masses of fluid were required to form the Elkhorn skarns. Both the stable isotope data and mass balance calculations presented here and in Bowman (ms) also indicate that skarn formation at Elkhorn was not a reciprocal or even local metasomatic process of chemical interaction between intrusion and carbonate wallrock restricted to a few meters of the intrusive margin. Rather, skarn formation involved mass transfer of significant masses of water and dissolved constituents over considerable distances through igneous rock and along the intrusive contact. These calculations imply that regardless of the ultimate origin of the skarn fluids, large quantities of both skarn fluid and igneous rock — relative to wallrock replaced — were involved in skarn formation at Elkhorn. These calculations further suggest that a mass of intrusion greatly in excess of that exposed in the aureole was involved in forming the skarn observed in the Black Butte aureole.

Apparently, even larger masses of fluid are involved in the formation of mineralized skarns. Isotopic data from the Pine Creek, Calif. (Brown, Bowman, and Kelly, 1985) and CanTung, Northwest Territories, Canada

(Bowman and others, 1985) skarns indicate that the minimum W/R ratios required for these tungsten mineralized skarns are, on average, 15 and 40, respectively. The lower W/R ratios estimated for the Elkhorn skarns are consistent with the more extensive development of gradients in compositional variables, including $X(CO_2)$, the general absence of mineralization, and the presence of three- and even four-phase assemblages in the Elkhorn skarns, compared to these other skarn systems (Bowman and Essene, 1984).

Skarn fluids appear to have interacted progressively with the high-^{18}O carbonate wallrock as they migrated up and out of the Black Butte stock, producing the progressive ^{18}O-enrichments and skarn mineral zonation observed in the skarns. Such interaction could have involved either isotopic exchange with the carbonate oxygen reservoir as a whole or mixing and exchange with the ^{18}O-enriched CO_2 evolved during initial decarbonation reactions. Mass-transfer calculations indicate that significant amounts of CO_2 evolved during the decarbonation reactions involved at the marble/skarn interface. This CO_2 likely mixed and isotopically exchanged with the H_2O-rich skarn fluids, generating both $X(CO_2)$ and $\delta^{18}O$ gradients within the skarns. The good agreement between petrologically defined $X(CO_2)$ limits for stage I skarn formation (0.02-0.30) and $X(CO_2)$ limits based on measured $\delta^{18}O$ values of skarn minerals (0.0-0.25) provides support for the importance of CO_2–H_2O mixing in skarn formation at Elkhorn. Taylor and O'Neil (1977) previously concluded that such a process was important in the formation of skarn at Osgood Mountains, Nev. as well. These two studies suggest that H_2O–CO_2 mixing may be a common and important mechanism in contact skarn petrogenesis. However, the oxygen isotope data indicate that skarn formation in both areas involved water-rich fluids, despite the evolution of significant quantities of CO_2 accompanying replacement of the carbonate wallrock.

There is at least an approximate correlation between isotopically and petrologically defined $X(CO_2)$ limits for individual skarn zones at Elkhorn. Both independent sets of data define progressive increases in $X(CO_2)$ away from the intrusive contact. This mixing process provides a realistic mechanism, at the physical-chemical conditions of skarn formation, for producing both the $\delta^{18}O$ variations and the $X(CO_2)$ gradients thought to be responsible for much of the observed mineral zonation within the skarns (Bowman and Essene, 1984). It should be emphasized, however, that additional compositional variables [$a(SiO_2)$, $f(O_2)$, $a(FeO_x)$, et cetera] are locally important in determining the petrologic characteristics of the skarns. The CO_2–H_2O mixing process can only be a generalization for a complicated geochemical process. It is a model in need of further testing.

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Appendix

Mass-balance calculations.—Depletions of ^{13}C and ^{18}O in calcite resulting from single-stage decarbonation accompanying transformation of marble to skarn were calculated from the relation (illustrated for carbon):

$$X(CO_2)\,(\delta^{13}C_{Cc(f)} - \Delta Cc\text{–}CO_2) + (1 - X(CO_2))\,\delta^{13}C_{Cc(f)} = \delta^{13}C \text{ system}$$

where: $X(CO_2)$ = mole fraction of CO_2 in the system and $\delta^{13}C_{Cc(f)}$ = final carbon isotope composition of calcite after any given stage of decarbonation. Carbon and oxygen isotope effects resulting from continuous decarbonation were calculated using the Rayleigh distillation relation (illustrated for carbon):

$$\delta^{13}C_{(f)} = (\delta^{13}C_{(i)} + 1000)f^{(\alpha_{CO_2\text{—}Cc} - 1)} - 1000$$

Where f = residual mass fraction of carbon (or oxygen) in the system.

The oxygen isotope effects of equilibrium mixing of magmatic H_2O and metamorphic CO_2 at 525°C were calculated from the mass-balance relationship:

$$\delta^{18}O_{H_2O(f)} = \frac{X_O^{H_2O}\,\delta^{18}O\,(H_2O)_i + X_O^{CO_2}\,\delta^{18}O\,(CO_2)_i - 8.7\,X_O^{CO_2}}{X_O^{H_2O} + 1.0087\,X_O^{CO_2}}$$

The $\delta^{18}O\ CO_{2(f)}$ and $\delta^{18}O$ system can easily be solved by use of the relationship:

$$\delta^{18}O\ (\text{system}) = X_O^{H_2O}\,\delta^{18}O\,(H_2O)_f + X_O^{CO_2}\,\delta^{18}O\,(CO_2)_f$$
$$= X_O^{H_2O}\,\delta^{18}O\,(H_2O)_i + X_O^{CO_2}\,\delta^{18}O\,(CO_2)_i$$

$X_O^{CO_2}$ and $X_O^{H_2O}$ are the mass fractions of oxygen in CO_2 and H_2O respectively, in the CO_2–H_2O mixture.

The mass ratios of oxygen in skarn-forming fluid (W) to that in host marble (R) which obtained during reaction of marble to skarn were computed using the relation (Taylor, 1971, 1974):

$$W/R = \frac{\delta^{18}O_{rock(f)} - \delta^{18}O_{rock(i)}}{\delta^{18}O_{H_2O(i)} - (\delta^{18}O_{rock(f)} - \Delta_{rock\text{—}H_2O})}$$

Values for rock-water oxygen isotope fractionations were estimated from measured mineral modes and the oxygen isotope fractionation data summarized in Friedman and O'Neil (1977). Equilibrium exchange was assumed. All W/R ratios should be regarded as minima because of the possibilities of incomplete exchange.

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