MAP SHOWING WORLD DISTRIBUTION
OF CARBON-DIOXIDE SPRINGS AND
MAJOR ZONES OF SEISMICITY

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GLOBAL DISTRIBUTION OF CARBON DIOXIDE DISCHARGES AND MAJOR ZONES OF SEISMICITY

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ABSTRACT

Carbon-dioxide discharges are concentrated along zones of seismicity such as the circum-Pacific belt and the alpine belt of southern Europe and Asia Minor. They commonly occur along young orogenic belts and are seldom found in either old orogenic belts or cratonic areas of continents except where the cratons are being fragmented. Submarine springs discharging CO₂ are known at only a few localities along oceanic crustal spreading centers, but these may indicate a highly common and widespread phenomenon. Geologic and isotopic data indicate that the CO₂ being discharged from these several tectonic settings is derived variously from (1) organic material, (2) metamorphism of marine carbonate rocks, and (3) the mantle. Production of CO₂ at depth may develop high pore pressure and thus facilitate slippage of faults. Rapid release of CO₂ may result in explosive activity.

INTRODUCTION

Carbon-dioxide (CO₂)-rich waters have long been of interest as early as 77 A.D., Plinius Secundus (LXXVII, Libra XXI) reported on springs at Tungri, which is the present-day spa, Belgium (Bostock and Riley, 1856), and on springs at Dorylai (Plinius Secundus, LXXVII, Libra VI), the present-day Eskisehir, Turkey (Bostock and Riley, 1887).

The production of CO₂-rich waters (commonly also rich in boron) by active metamorphism of carbonate-bearing rocks at depth was first suggested by White (1957). Water must be driven off because metamorphism at high temperature generally is accompanied by dehydration. Many rocks undergoing metamorphism contain carbonates and silicates that may react to release CO₂. Organic material may also be a source of CO₂ and hydrocarbon gas. Two fluid phases escape under lithostatic pressure gradients, a water-rich liquid (high in bicarbonate, boron, and other constituents) whose Table 1 composition is near zero per mil and whose hydrogen composition is in the range -30 to -60 per mil, and a CO₂-rich vapor that may contain large amounts of hydrocarbon gases and H₂S. Because the metamorphic gas and water steam from different reactions, they may be generated at the same time or at different times. CO₂ is likely to be the most notable metamorphic constituent in surface effluents, occurring either as CO₂-rich vapor or as anomalously large amounts of bicarbonate dissolved in water. The CO₂ vapor commonly discharges through meteoric water. Metamorphic water is also commonly discharged at the surface as springs. It is recognizable even if somewhat diluted with meteoric water (White, Barnes, and O'Neil, 1973) because the metamorphic water is so anomalous in chemical and isotopic composition (Barnes and others, 1981). The presumed metamorphic water is thought unlikely to be diluted by meteoric water where pressures are lithostatic, because the meteoric waters would have to flow against the gradient; however, dilution probably is extensive at hydrostatic pressures. Mixing of metamorphic and meteoric waters is suspected if the concentration of chloride is high or where contents of bicarbonate and boron are large even though the isotopic composition is similar to that of meteoric water. Metamorphic water in amounts of less than 10 percent may not be detected isotopically in a mixture of metamorphic water and meteoric water.

CO₂ discharges in California were shown to be related to certain lithic provinces and major faults (Barnes, Irwin, and Gibson, 1975). Aseismic movement (creep) along certain segments of the San Andreas fault probably is related to high CO₂ pressures or to structurally diverted CO₂-charged water (Irwin and Barnes, 1975). Recognition of an apparent relation between CO₂ discharges and seismicity led to a preliminary report and map showing the global distribution of the two phenomena (Barnes, Irwin, and White, 1978). Following this early compilation, much additional data regarding the distribution of CO₂ discharges has been obtained, particularly from Afghanistan, China, and Peru. More information on the distribution and isotopic composition of gases emitted from submarine thermal centers has become available.

For our compilation, a CO₂-rich discharge is defined as that of a gas containing more than 90 percent CO₂ by volume, which is likely to be the most notable discharges and seismicity in Australia (except for the Holocene volcanic field of Victoria) and in most other major old orogenic belts or cratonal areas of continents. In both areas the geographic coincidence with major zones of historical seismicity is generally striking. Isolated CO₂ discharges also tend to occur in locally seismic areas. Zones of CO₂ occurrences coincide with some orogenic zones containing ultramafic rocks and blueschist-facies rocks, but in old orogenic zones such as the Urala and the Appalachians, CO₂ discharges are generally absent. Equally impressive is the general absence or scarcity of CO₂ discharges and seismicity in Australia (except for the Holocene volcanic field of Victoria) and in most other major old orogenic regions of the world. The similarity in distribution of CO₂ discharges and zones of seismicity suggests that the production of CO₂ is related to fundamental tectonic processes that are operating widely at the present time. Some CO₂ discharges, however, are near young or active volcanoes, and in regions of high heat flow. Submarine discharges of CO₂ have been discovered at a few places along crustal spreading ridges, such as near the Galapagos Islands and at the Loihi Seamount, (Hawaiian Islands), and similar occurrences may be more commonplace than now recognized.

Both the CO₂ discharges and the seismic epicenters are concentrated mainly along or near the boundaries of major crustal plates and probably result from the interaction of the plates. It is along these active plates that the resistance to plate motion is expressed as seismic energy and anomalous temperatures. Where plates are divergent, conditions are appropriate for release of CO₂ from marine carbonate-bearing rocks through processes of subduction, metamorphism, and igneous intrusion. Where plates are convergent as along mid-ocean ridges, the CO₂ escapes from the mantle. In addition, continental fractures extending to sufficient depth may also yield CO₂ from the mantle as along the Rio Grande...
rift zone, the East African rift zone, and the cratonic rocks of St. Lawrence valley of eastern Canada. Within these tec-
tonically active zones, carbon dioxide is being discharged from
rocks as old as Precambrian and as young as Holocene.
The generation of CO₂ is a long-term event compared to the
historical record of seismicity, and thus may be a useful
parameter for regional seismic zoning. In old cratonic regions
the general absence of both CO₂ discharges and seismicity
indicates the continuance of a long history of tectonic quiescence
in those regions. Old cratonic areas may overlie areas of the
mantle depleted of carbon dioxide and hence nonconve-

**ORIGIN OF CO₂**

Throughout the world, CO₂ issues from metamorphic
rocks as well as from rocks that have no metamorphic his-
story. The CO₂ is thought generally to come from three dif-
ferent sources: (1) organic material, (2) metamorphism of
marine carbonate rocks, and (3) the mantle. Stable-isotope
data are helpful in identifying the sources of CO₂, especially
where there is no evident near-surface source. Organic
material, in the form of coal, fossil wood, and petroleum, is
rather depleted in δ¹³C (carbon-13) such materials usually
contain less than -20 per m il (Craig, 1953). The δ¹³C iso-
otope composition of marine carbonates is approximately 0 per m il
relative to the PDB (Peedee belemnite) standard (Craig, 1953).
Direct evidence for the isotope composition of CO₂ from
mantle sources is provided by inclusions in volcanic
rocks erupted along spreading ridges. Moore and others (1977)
reported δ¹³C values from -2.6 to 0.5 per m il for CO₂ inclusions
in tholeiitic rocks from the mid-Atlantic Ridge. Other situations
thought to provide direct evidence of isotopic composition of
mantle-derived CO₂ are the discharges at crustal spreading centers and at mantle plumes.

The chemical criteria for the CO₂ discharges are arbi-
trary, but during the course of the compilation it became
obvious that changing the concentration limits to values as
low as 0.5 g/L (still an unusually high HCO₃⁻ concentration)
would serve no purpose other than to provide more occur-
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would not change the general pattern of occurrences.

The authors would appreciate receiving additional information
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**MAP COMPILATION**

The chemical criteria for the CO₂ discharges are arbi-
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The sources of data for the CO₂ discharges are given separately
from the references cited in the text. For uniformity all
sources of data have been translated into English. The
authors would appreciate receiving additional information
on the location and the chemical and isotopic composition of
CO₂-rich waters.

The CO₂ occurrences and the major zones of seismicity are
compiled on a base map that shows the global distribution of
alpine-type ultramafic rocks and blueschists (Irwin and
Coleman, 1972). Additional blueschist localities are from N.
L. Dobretsov (written commun., 1973). It should be noted
that the zones of seismicity are generalized from Tarr (1974),
with the exception of data from Fairhead and Henderson
(1977) for Africa, Lee and others (1978) for China, and NOAA
(1970) for the north polar region. Tarr's (1974) map shows
only magnitude-5 and greater earthquakes and is restricted to
the period 1963-72. A more inclusive and lengthy record of
seismicity would show an even closer correlation with the
CO₂ discharges.
A roughly continuous belt of CO₂ discharges, more than 30,000 km long, stretches from southern South America through Central America, western North America, Kamchatka, and New Guinea to New Zealand along the circum-Pacific belt.

In the Mt. Hiroshi area of Japan, CO₂ discharges associated with earthquakes have been documented by Yoshioka and others (1970). In the same area, Wakita and others (written commun., 1977) reported δ¹³C values from -1 to -3 per mil and interpreted the source of the CO₂ to be Paleozoic marine carbonates. Wakita and others attributed the high value of 8.9 X 10⁻⁶ for the He/He ratio for the He in the CO₂ to a mantle-derived source. They interpreted the He to be derived from a small intrusion into the crust accompanied by reactions with marine carbonates to yield CO₂.

On the Alaska Peninsula at Gas Rocks (57°31'40"N, 158°30'00" W), an explosive volcanic event began in April 1977 that yielded an alkali olivine melt inferred to have come from the mantle (Kienle and others, 1980). In August 1977 the copious gas discharge near Gas Rocks was sampled. The gas was 98 percent CO₂ and its δ¹³C composition -6.36 per mil (Barnes and McCoo, 1978). The content of δ¹³C is too low for a marine-carbonate source but is in the range of values for CO₂ from isolated intrusions. The explosive event was described by McKnight (1979), who attributed some of the CO₂ to the magma chamber in which the pressure of CO₂ dissolved in the melt exceeded the total confining pressure.

The broad belt of CO₂ discharges of the Western United States may be subdivided into three sub-belts: (1) a coastal (Franciscan Complex) geochemical province, (2) the Sierra Nevada, and (3) the Rocky Mountains.

Franciscan rocks of the coastal geochemical province discharge CO₂ (Barnes, 1970) generally accompanied by methane (Presser and others, 1976). A current study shows that CO₂ from Franciscan rocks has δ¹³C values that range from +5.2 to -14.0 per mil. The data at hand show no relation between the δ¹³C data and the existence of travertine deposits or the presence of methane in the gases. The CO₂ is apparently generated both by the breakdown of organic material depleted in δ¹³C and by solution or metamorphism of calcite of marine origin enriched in δ¹³C. If the mantle also contributes to the CO₂ flux, its contribution is masked by mixtures of CO₂ from other sources. The present phase of metamorphism of the Mesozoic eugeosynclinal sedimentary rocks of the Coast Ranges of California is probably in its early stages, even though the rocks were previously metamorphosed. Labile organic materials are still present and decomposed to be metamorphosed is also accompanied by quite high heat flow.

CO₂ discharges from localities in the Sierra Nevada show δ¹³C values of -6 to -10 per mil (Barnes and others, 1981). Chemical and isotopic evidence indicates that the fluids are meteoric water that contains CO₂ from the mantle. In order for CO₂ to escape, it must be present as a separate phase in the mantle, and it must exist as a separate phase to at least a shallow a depth as the meteoric water circulates. To be present as a separate phase, the CO₂ pressure must be at least equal to the confining pressure.

In the Rocky Mountains province in Colorado, CO₂ species in CO₂-rich springs have been analyzed for δ¹³C (Presser and others, 1981). The δ¹³C-enriched CO₂ (-2.0 to -6.9 per mil) found at Rico may be from the metamorphism of shaly limestone and the mantle. The CO₂-rich springs at Rico (Hedgpeth, 1974), or from deeper sources. Impure marble that is part of a Precambrian metamorphic complex occurs near Guffey (D. S. Sheridan, oral commun., 1977). The δ¹³C value of -1.4 per mil in the CO₂ discharging near Guffey may be from the metamorphisms of the marble. CO₂ discharges from the Precambrian Pikes Peak Granite at Manitou Springs (-3.3 to -2.8 per mil) possibly are from a mantle source. If so, mantle-derived CO₂ may be more enriched in δ¹³CO₂ than indicated earlier. δ¹³C data from complex igneous and metamorphic terranes cannot be unequivocally interpreted without a detailed geologic study and consideration of multiple origins.

Yellowstone National Park, Wyoming, is a region that includes several localities of CO₂ discharge and is also noted for extraordinarily high heat flow (Fournier and others, 1976). The two phenomena do not always coincide perfectly, however. For example, heat flow in excess of 2 heat-flow units, or at least 30 percent above the world's average conductive heat flow, characterizes most of the broad central and western part of the United States (Barnes and others, 1975, plate 1), but CO₂ occurrences are no more abundant there than in adjacent areas to the east and north. Conductive heat flow is slow relative to fluid flow. Thus, a thermal anomaly at depth may be a source of CO₂ that is discharged at the surface before an increase in heat flux at the surface is noted.

Craig (1961) reported isotope analyses on the CO₂ from Yellowstone National Park in which δ¹³C values range from -1 to -6 per mil and averages (13 samples) -2.8 per mil. Although the average δ¹³C composition is rather close to what would be expected for an average marine limestone, considerable volcanic or mantle CO₂ may be present. Friedman (1970) studied travertine that is presently forming in Yellowstone National Park and reported that fractionations between dissolved carbon species and travertine range from near equilibrium (4 per mil) at 75°C to a disequilibrium fractionation of only 1 per mil at 25°C. Neither Craig nor Friedman, however, measured the isotope fractionation between dissolved CO₂ species and CO₂(gas). In the Sierra Nevada and Klamath Mountains of California, Barnes and others (1981) studied the fractionation between dissolved CO₂ species and CO₂(gas) from the springs. They found that fractionation ranges from equilibrium (4 per mil) down to no fractionation (0 per mil) over the temperature range 35°C to 40°C. Some small fractionations of the source of the Yellowstone CO₂ gases to be identified as limestone (Craig, 1953), and led Friedman (1970) to conclude that dissolved CO₂ species and travertine of Yellowstone National Park are derived from marine limestone by decarbonation. Similarity of lead isotopes in the limestone and travertine also points to the limestone as the source for the travertine (Leeman and others, 1977).

Studies of gases and waters near and in Mount St. Helens show that the volcano is full of steam (85 percent) and other gases, chiefly CO₂ (Evans, Banks and White, 1981). The steam is from metamorphic brine in the underlying Tertiary Ohanapeechee Formation (Barnes and others, 1981). Prior to the May 18, 1980 eruption, CO₂ with δ¹³C values of -19 per mil issued from the volcano; after the eruption, however, values of -10 to -11 per mil were found as the proportion of mantle-derived CO₂ exceeded that from the breakdown of organic material.

In summary, the scattered CO₂ discharges of the circum-Pacific belt seem generally to be derived from metamorphism of carbonate-bearing rocks and from mantle sources. Some widely separated occurrences may be related to isolated intrusions that have caused decarbonation.

EUROPE AND ASIA MINOR

The CO₂ that is discharging from localities in Europe and Asia Minor is derived in large part from metamorphism of marine carbonates, whether from originally impure limestone or from calcareous siliceous sediments. A marine carbonate origin for the CO₂ of the mineral waters of Czechoslovakia was suggested by Barnes and O'Neil (1976) on the ground that δ¹³C values of the high-CO₂ waters are close to 0 per mil. The CO₂-rich waters discharging in Czechoslovakia show deuterium and δ¹⁵N compositions (Barnes and O'Neil, 1976) that are in excellent agreement with the stable-isotope relations of meteoric water (Craig, 1961). The isotopic results confirm the conclusions of Kacura and others (1969), based on hydrologic analysis, that the waters are meteoric. Doudle and others (1973, 1975) showed that much of the CO₂ from Polish mineral waters probably derives from oxidation of organic matter. The δ¹³C data of Buschide and Buschide (1976) show an average value near 0 per mil and indicate that the CO₂ of the Caucasus is probably also derived from marine carbonates. Comides and Keeskes (1974) concluded from δ¹³C data that the CO₂ of Hungarian mineral waters was derived partly from metamorphism of limestone and partly from
volcanic sources. By measurements of the isotopic compositions of French mineral springs, Batard and others (1982) showed that the water is of meteoric origin but the \( \text{CO}_2 \) is largely of igneous (mantle?) origin. In a thorough study of the isotopic compositions of \( \text{CO}_2 \) in central and southern Italy, Panichi and Tongiorgi (1976) showed that most of the \( \text{CO}_2 \) is from metamorphism of carbonate rocks. Their isotopic data agree with the results separately reported by Manfra and others (1974). Craig (1963) showed that the waters from Lardarello, Italy, are also chiefly of meteoric origin, but with enrichments in \(^{18} \text{O} \) owing to reaction (exchange) with the rocks.

The lack of identified metamorphic or magmatic water accompanying the \( \text{CO}_2 \) is puzzling. Possibly water that was present earlier either has escaped or has been incorporated in hydrox minerals. Conceivably, metamorphic water does not reach the surface because after it condenses it is no longer buoyant, or, if it escapes, it may be diluted beyond recognition by meteoric water, as in the Sierra Nevada, Calif. (Barnes and others, 1981). The observation of large-scale exchange of \(^{18} \text{O} \) between igneous rocks and meteoric waters (Taylor, 1974; Margaritz and Taylor, 1978) is consistent with the failure to find metamorphic water in Europe or Asia Minor.

In Europe, the belts of \( \text{CO}_2 \) discharge correlate approximately with high heat flow, not only in the Precambrian basin of central Europe but also to the east and west. The high heat flow in the Caucasus and the Crimea (Petkov and others, 1976) corresponds quite well with the occurrence of \( \text{CO}_2 \) discharges. To account for the high heat flow of the Pannonian Basin, Stegenas and others (1975) advocate mantle-derived fluids intruding into the overlying sediments. They stated that the high heat flow cannot be supported by thermal conduction. Lachenbruch and others (1976) pointed out that intrusion is not as effective in transferring heat as convective flow in a melt. However, once the melt stops convecting, heat flow decreases until a more normal thermal gradient is established. Convective heat flow and the long subsequent time necessary for recovery may explain why older metamorphic terranes such as the Appalachians and the Urals show so little evidence of fluids derived from present-day metamorphism. Saratoga Springs, New York, is the only discharge of \( \text{CO}_2 \) known in the Appalachians, and none is known in the Urals.

Further evidence for metamorphic reactions in the Roman province was supplied by Hurley and others (1966). On the basis of the \(^{13} \text{C} / {\text{C}}_{12} \) ratio and the \( \text{Rb} \) and \( \text{Sr} \) contents of potash-rich lavas, they concluded that the lavas are derived from the melting of old sialic crustal rocks. Turi and Taylor (1978) concluded from \(^{18} \text{O} \) compositions that the volcanic rocks of the Roman province have undergone moderate to extensive reactions with crustal material, but are at least in part derived from the mantle.

CONCLUSIONS

Regional metamorphism, perhaps in early stages, is probably occurring now in California in eugeosynclinal rocks and their attendant ultramafic rocks. Regional metamorphism, perhaps of a more advanced stage, is occurring in Europe and Asia Minor, where the \( \text{CO}_2 \) production is principally from the breakdown of calcite of marine origin. Oldest terranes such as the Appalachian and Ural orogenic belts may be products of metamorphism of the type now occurring in Europe and Asia Minor.

Relatively isolated metamorphism may be occurring within a belt from South America to New Zealand, perhaps related to contact metamorphism associated with intrusions. The areal extent of \( \text{CO}_2 \) production in Europe and Asia Minor is much greater than that in any area found along the circum-Pacific belt with the possible exception of the Western United States. Judging from the \( \text{CO}_2 \) occurrences, if any areas of the world are undergoing regional metamorphism at the present time, they are the orogenic belts of Europe and Asia Minor and the Coast Ranges of California. Many of the rocks that are being metamorphosed have already undergone metamorphism one or more times.

Crustal spreading centers are also the loci of \( \text{CO}_2 \) discharges, and the isotopic composition of their discharges is thought to indicate mantle origin. Discharges of \( \text{CO}_2 \) from volcanic centers are sometimes accompanied by seismicity and eruption of lava, and at other times the discharges are aseismic and consist only of gas. It is unlikely that the aseismic discharge of \( \text{CO}_2 \) is caused by upward movement of magma to lesser depths where degassing occurs. More likely, it is caused by degassing of the mantle, which perforce must contain a separate \( \text{CO}_2 \) phase in addition to the silicates.

At no pressure or temperature is \( \text{CO}_2 \) as dense as the silicate minerals that make up the mantle (Kennedy and Holzer, 1966), and volumes of mantle that contain \( \text{CO}_2 \) must therefore be buoyant. The buoyancy provides a mechanism for upward movement of magma which, being \( \text{CO}_2 \) saturated, will degas as pressure decreases. Thus, the \( \text{CO}_2 \) is both a causal agent of the upward movement of magma and a product of the degassing that results from the upward movement.

The occurrence of \( \text{CO}_2 \) discharges along crustal spreading centers may also indicate a causal relation in that the buoyancy of gas-charged melts may well be responsible for mantle convection and resulting seafloor spreading.

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**PERU**


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UGANDA


UNION OF SOVIET SOCIALIST REPUBLICS


UNITED KINGDOM


UNITED STATES


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