general agreement with band calculations, but the bands near the Fermi level were not in agreement with calculated normal-state, one-electron bands (*13*, *14*). (Those band-mapping studies had inadequate resolution for the study of Fermi edge effects.) The orientation of our sample was such that our spectra sample a region in **k**-space not along a symmetry line, hence not displayed in band calculations. These points are shown in Fig. 3 [from Massida *et al.* (*13*)], where it can be seen that they are, indeed, near bands that pass through the Fermi level. The states at the Fermi level are, from the calculation (*13*) a mixture of O-2*p* and Cu-3*d* at the points labeled a and b in the Fig. 3, O-2*p* and Bi-6*s* and 6*p* around the point e, while in the shaded region, Bi-6*s* and *p* states are hybridized with the Cu and O states. A recent angle-integrated photoemission study (*15*) showed that at the Fermi level, the states are about 35% Cu-3*d* and 65% O-2*p* in character, a conclusion different from that of earlier studies (*12*, *16*). In an angle inte grated study, the anticipated Bi component will be difficult to identify, if present. At 18° we are near two calculated bands at the Fermi level, one with a Bi component, but this measurement is not sufficient to confirm the Fermi surface. It is clear that more data are needed to determine if the electronic structure of this material is well described by the band calculations, and with the small Brillouin zone, higher angle resolution (*2*), with no loss of energy resolution, is desirable. The observed peak and its temperature dependence appear not to be consistent with what is expected to date for photoemission from a resonating valence bond (RVB) model (*17*). Above T_c this model appears to predict, for an angle-integrated EDC, an edge similar to a Fermi edge, but of different slope, and displaced from the position of the Fermi edge by an amount depending on the maximum spinon energy. Our comparisons of the Fermi edges of Pt and $Bi_2Sr_2CaCu_2O_8$, the latter in an angle-resolved EDC, indicate no relative shift of the edges above T_c. No RVB predictions for photoemission below T_c have appeared in the literature.

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Origins and Movement of Fluids During Deformation and Metamorphism in the Canadian Cordillera

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Stable isotope data from quartz veins in the Canadian Cordillera indicate that crustal fluids were heterogeneous in terms of sources and flow paths during Mesozoic-Cenozoic metamorphism and deformation. In regions of strike-slip and extensional faulting, the fluid regime to depths of at least 15 kilometers was dominated by convected, chemically evolved meteoric water. In contrast, in thrust faulted regions, the fluid regime was dominated by fluids derived from metamorphic devolatilization reactions. Deep convection of meteoric water implies that fluid pressures are hydrostatic in such systems not lithostatic, as had been commonly assumed. The occurrence of significantly lower fluid pressures would necessitate reevaluation of the manner in which metamorphic phase equilibria and stress relations in the crust are modeled. In addition, this study indicates that mesothermal gold deposits in the Canadian Cordillera are a product of the meteoric water convection process.

THE EXTENT OF PENETRATION OF surficial waters into the crust is a key question in studies of fluids in the earth's crust (*1*). Calculations of the probable depth of convection of surficial fluids (*2–4*) have shown that in rock units with bulk permeabilities of 10^{-17} m^2 or greater, fluids originating at the surface can move by free convection under a normal geothermal gradient. Data of Brace (*5*, *6*) suggest that permeabilities in excess of 10^{-17} m^2 are common in the brittle crust, especially in units that have undergone even minor amounts of fracturing. Permeabilities on the order of 10^{-16} m^2 have been observed to depths of 10 km in the Kola deep hole in the Soviet Union (*7*). These results indicate that convection of surface waters should be common in the brittle crust, providing that there is a high degree of vertical interconnectivity of fractures. Fluid pressures in petroleum exploration and development wells in actively subsiding sedimentary basins in the U.S. Gulf Coast and elsewhere, however, commonly exceed the hydrostatic head for that depth (*1*). The presence of these overpressured zones prevents the influx of surface waters. These results have been thought by many to indicate that surface fluids only penetrate a few kilometers into the crust and that the dominant source of deeper fluids in the crust is from expelled pore fluids at shallow depths and from diagenetic or metamorphic devolatilization reactions at greater depths (*1*, *8*). Unresolved as yet, however, is the question of how generally applicable to other geological settings is the depth–fluid pressure relation observed in these subsiding basins.

The recognition that crustal fluids differ in oxygen and hydrogen isotopic ratios has permitted the common use of stable isotopes to identify the types of fluids involved in various geological processes. Isotopic ratios of meteoric water (rain and snow) vary with latitude and elevation, lower $\delta^{18}O$ and δD contents being indicative of higher latitudes or elevations or both (*9*) (Fig. 1). Isotopic values for waters produced by metamorphic or magmatic devolatilization processes are typically less variable and relatively enriched in ^{18}O and D (Fig. 1) (*10*). Stable isotope studies of both in-place and obducted samples of the oceanic crust (*11*, *12*) have clearly documented that extensive convection of sea water occurred in the oceanic crust to depths of at least 5 km. Recently, evidence of deep convection of sea water also has been obtained from metamorphosed, continental crustal rocks in the Pyrenees (*13*). The convection of meteoric water in and around igneous plutons in the continental crust has been documented by the work of Taylor and co-workers (*14*). They have shown that the heat of cooling

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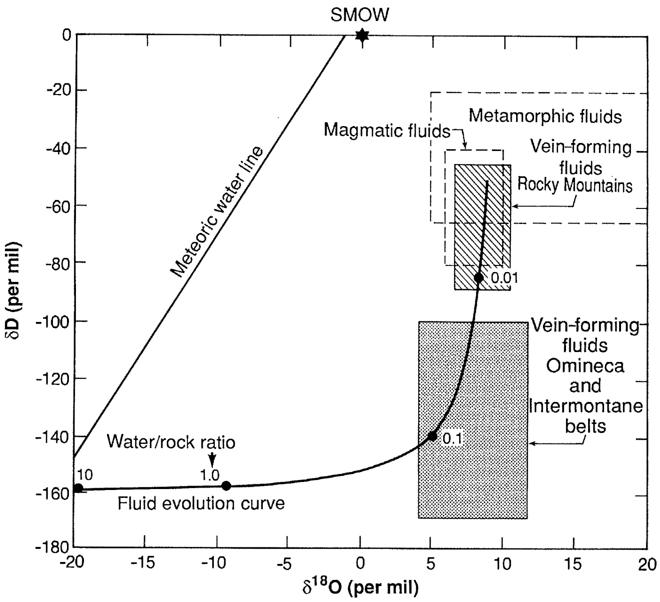


Fig. 1. A δD versus $\delta^{18}O$ diagram depicting typical ranges of isotopic values for various crustal fluid reservoirs (*10*). The fluid evolution curve depicts changes in water isotopic chemistry with decreasing w/r values. The representative curve was calculated for a temperature of 400°C, rocks of intermediate composition between felsic plutonic and sedimentary rocks, and the equations of Field and Fifarek (*28*). The patterned areas indicate the range of calculated values for veins in the respective locations; SMOW, standard mean ocean water.

plutons can drive meteoric water convection systems that are tens of hundreds of square kilometers in areal extent and 1 to 15 km deep. However, apart from those systems localized around plutons, questions remain as to the extent and importance of regional meteoric water convection in tectonically active parts of the continental crust.

The Canadian Cordillera provides an excellent site to evaluate the sources and evolution of synorogenic fluids. The Canadian Cordillera is divisible into five physiographic belts: the Rocky Mountain, Omineca Crystalline, Intermontane, Coast Plutonic, and Insular belts (Fig. 2). The Rocky Mountain and Omineca Crystalline belts are separated by the Rocky Mountain–Tintina trench system. The five belts are composed of a series of autochthonous and allochthonous, oceanic and island arc terranes (*15*). Accretion of the allochthonous terranes of the Intermontane and parts of the Omineca belts during the Middle Jurassic resulted in extensive metamorphism and deformation in the Omineca Crystalline belt. During the Cretaceous, allochthonous terranes of the Insular belt were sutured to North America resulting in much of the deformation, metamorphism, and plutonism in the Coast Plutonic belt. Subsequent to the accretionary events, northwest-trending, dextral, strike-slip faults displaced large segments of the accreted terranes northward relative to North America (*16*). This was closely followed by Eocene extension and metamorphism in southcentral British Columbia (*15*). The peak of thrusting and metamorphism affecting the autochthonous units of the Rocky Mountain belt occurred during the Late Cretaceous and Early Tertiary. Because deformation and metamorphism occurred at relatively northern latitudes, there were distinct differences between the $\delta^{18}O$ and δD signatures of meteoric and metamorphic fluids. In addition, due to regional differences in tectonic style in the Cordillera—thrusting in the Rocky Mountains to the east of the Rocky Mountain trench and thrusting followed by strike-slip and extensional faulting in the Omineca to the west of the Trench—the Canadian Cordillera provides an ideal site to investigate differences in structural control of fluid flow.

Our sampling was concentrated in the Rocky Mountain and Omineca belts (Fig. 2). Samples of quartz ± carbonate veins and host rocks were collected from greenschist to lower amphibolite facies units. Approximately 40% of these samples came from sites of anomalous gold concentrations. Special emphasis was placed on sampling quartz ± carbonate veins because these features are generally believed to represent fluid pathways that were active during or slightly after deformation and metamorphism (*8, 17*). In addition, vein quartz typically hosts fluid inclusions, which are microsamples of the fluid that deposited the vein (*18*). The fluids contained in the inclusions are the only direct means of studying synorogenic fluids. Fluid inclusion studies on samples from quartz veins in some of the sample areas (*19*) indicate that the minimum temperatures of vein-forming fluids were 250° to 300°C, the minimum pressure was 0.1 GPa, and the $CO_2/(H_2O + CO_2)$ ratios by mass were 0.005 to 0.20.

Systematic differences in the $\delta^{18}O$ compositions of vein quartz were observed in veins from differing geological settings (Fig. 3A). The $\delta^{18}O$ values for quartz veins in greenschist terranes range from +11 to +20 per mil with a mean of +15.5 ± 3.0 per mil (number of samples, n = 119) (*20*). This range and mean are typical of values from quartz ± carbonate veins in greenschist facies metamorphic rocks worldwide (*21*). Quartz veins in amphibolite facies units all have $\delta^{18}O$ values less than +10 per mil; $\delta^{18}O$ values for quartz veins in low-temperature, Hg- and Sb-bearing veins are all greater than +20 per mil.

The relatively wide range in $\delta^{18}O$ values observed is at least partially a function of the range of temperatures at which the veins formed. Because the fractionation of ^{18}O versus ^{16}O between water and quartz decreases with increasing temperature (*22*), the difference between the $\delta^{18}O$ values of vein quartz and the fluid from which it precipitates increases with decreasing temperature of formation. Consequently, the calculated $\delta^{18}O$ values for vein-forming fluids span a more restricted range of values than the $\delta^{18}O$ results of the vein quartz. For temperatures of 400°C for amphibolite facies veins, 300°C for greenschist facies veins, and 200°C for Hg-Sb veins, calculations (*22*) yield a range of $\delta^{18}O$ values of H_2O in the vein-forming fluids of +4 to +12 per mil (Fig. 1).

There is a large variation, −30 to −160 per mil, in δD values of inclusion fluids (Fig. 3B). In contrast to the $\delta^{18}O$ results, there is no relation between variations in δD and temperature of deposition. However, there is a regional variation in values. All measured inclusion fluids, as well as associated serpentinites (*19*) from the Omineca Crys-

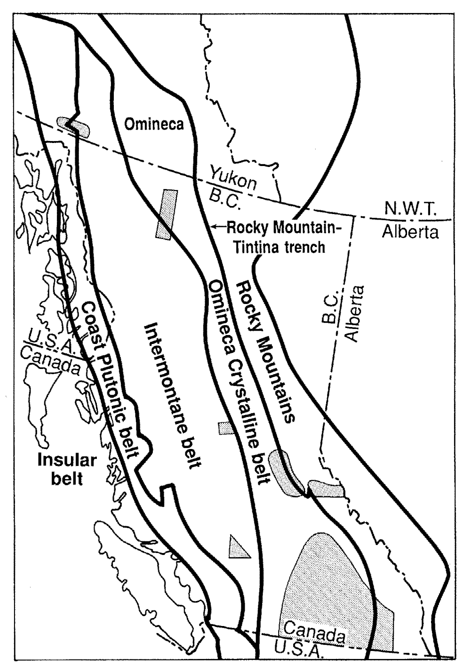
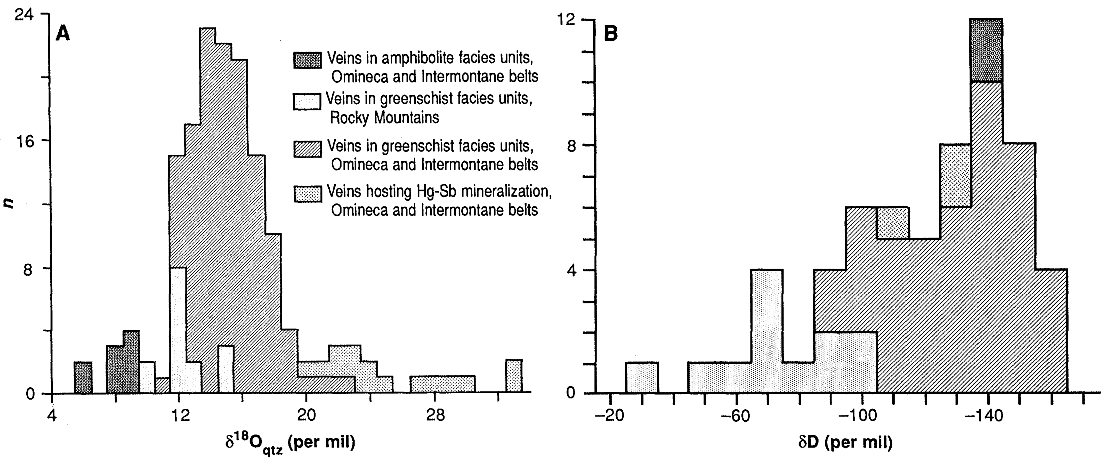


Fig. 2. Map indicating the regional distribution of physiographic belts in the Canadian Cordillera. Patterned areas indicate regions where most of the samples were collected.

Fig. 3. (**A**) Histogram depicting the results of the $\delta^{18}O$ studies of vein quartz (qtz) from veins in the indicated settings. (**B**) Histogram depicting the results of the δD studies of inclusion fluids from quartz veins in the indicated settings; *n*, number of samples.



talline belt and regions farther west have δD values that are less than -90 per mil. In addition, δD values decrease from south to north. On the other hand in the Rocky Mountains, δD values from inclusion fluids in quartz veins are distinctly enriched in D ($\delta D > -100$ per mil), relative to values in the Omineca belt. A regional distribution of values is noted in the Rockies with the most enriched δD values occurring in biotite grade metamorphic rocks in the western portions of the Rockies and more depleted values occurring in lower grade rocks to the east.

An important concern in analyses of inclusion fluids is the extent to which later, non–vein-forming fluids are present as secondary inclusions in the quartz and have contaminated the primary δD signal (*23*). Secondary fluid inclusions are common in nearly all quartz veins analyzed. We have suggested, based on textural evidence, that the majority of these secondary inclusions are the result of later stage events in the overall vein-formation process (*24*). The isotopic data support this interpretation. The consistently high δD values in veins in the Rocky Mountains, where local meteoric water is on the order of $\delta D = -130$ to -150 per mil, indicate that widespread contamination by shallow meteoric water has not occurred in these veins. Because veins in the Omineca and Intermontane belts are macroscopically and microscopically identical to veins in the Rockies, it is unlikely that shallow meteoric water contaminated the δD results of the veins of the Omineca and regions farther west.

The generally accepted model for the origin of fluids that formed quartz ± carbonate veins in greenschist facies rocks has been one of derivation by metamorphic devolatilization reactions (*1, 8, 17*). This interpretation was largely based on $\delta^{18}O$ values from vein quartz and the presence of the veins in metamorphic rocks. Calculated $\delta^{18}O$ values for the fluids that formed the veins in the Canadian Cordillera are similar to values observed in other studies and are typical of what are considered to be metamorphic values (*21*). However, the δD values obtained from the veins are not compatible with derivation by metamorphic devolatilization and are consistent only with the involvement of meteoric water. Earlier studies of D/H ratios from similar veins elsewhere have not documented the involvement of meteoric water because these studies were conducted at lower latitudes where the δD values of meteoric water are indistinguishable from those of metamorphic and magmatic fluids (*21*).

Even though the δD values of inclusion fluids in many of the veins in the Cordillera are consistent with the involvement of meteoric water (Fig. 1), the $\delta^{18}O$ values are substantially enriched in ^{18}O relative to meteoric water. Such ^{18}O enrichments are the result of interaction of the fluids with rocks as the fluids move through the crust (*14*). If the water to rock (w/r) mass ratio is high, on the order of 10 or greater, then the stable isotope composition of the fluids shifts only slightly during water-rock interaction. As the w/r ratio decreases, the $\delta^{18}O$ of the fluids increases, because of isotopic exchange between the fluids and the rocks. Because of the low hydrogen content of most rocks, only at a low w/r ratio does the δD value of the fluids increase. The observed values of δD and $\delta^{18}O$ in the vein-forming fluids in the Omineca Crystalline belt are consistent only with a derivation from meteoric water that has undergone water-rock interaction at low w/r ratios.

In contrast to the results from the Omineca Crystalline belt and regions farther west, the stable isotope results from veins in the Rocky Mountains span a range from typical metamorphic or magmatic values in the west to values between metamorphic and local meteoric values in the east. A magmatic origin for high δD values can be ruled out because plutons are absent in the area. The observed trend can be accounted for either by metamorphic fluids dominating in the higher metamorphic grades to the west and mixing with meteoric water in the east or by meteoric water undergoing water-rock interaction at very low w/r values. Either model is possible given the available data, but mixing of metamorphic and meteoric waters is considered to be more probable.

The differences in δD characteristics of vein-forming fluids between the Omineca Crystalline belt and the Rocky Mountains cannot be a function of differences in metamorphic grade, age of metamorphism, type of host rocks, or allochthonous versus autochthonous terranes because all of these parameters, to some extent, are similar in both regions. The only substantial difference between the two regions is in structural style. Thrust faulting was dominant in the Rocky Mountains, whereas early thrust faulting followed by strike-slip and extensional faulting characterized the Omineca belt (*15*). In strike-slip and extensional faulted regions, faults are generally steeply inclined. Such an orientation for major fault patterns provides large-scale zones of vertical, interconnected fracture systems permitting the deep penetration of surface fluids into the brittle crust. The most likely limit on depth of penetration for these fluids is the brittle-ductile rheological transition. Fluids produced by metamorphic devolatilization in vertically faulted systems would be overwhelmed by the greater flux of meteoric water (*19*). In contrast, thrust faulted terranes such as the Rocky Mountains are characterized by low-angle faults and in many areas, sedimentary units of variable permeability. This horizontal orientation of faults and stratigraphy probably results in alternating zones of high and low permeability, which severely inhibit influx of surface fluids and create conditions in which metamorphic fluids may dominate the fluid regime.

Our data indicate that the origins and movement of fluids in the continental crust are much more variable and dynamic than previously thought. The recognition of the existence of deep convection of meteoric water during regional deformation and metamorphism has important implications for models of the behaviour of fluids in the crust.

Synorogenic fluid pressure (P_F) often is assumed to equal lithostatic pressure (P_L), the pressure generated by the weight of the overlying column of rock (*1, 8*). In order for surface waters to convect, P_F must be approximately equal to hydrostatic pressure (P_H), the pressure generated by the weight of a column of water (*2*). Since P_H is always less than P_L, then under hydrostatic conditions, P_F is less than P_L. At a depth of 10 km, P_H = 0.1 GPa and P_L = 0.3 GPa, a substantial difference between fluid and rock pressures, reflecting the differences in density of water and rocks.

In metamorphic petrology, the assumption of $P_F = P_L$ is widely applied in the calculation of metamorphic phase equilibria (*1, 25*). In areas where $P_F \approx P_H < P_L$, such calculations would have to be revised to account for the lower P_F. Low fluid pressures will result in devolatilization reactions occurring at lower temperatures than if $P_F = P_L$. Consequently, under such conditions, isograds based on devolatilization reactions are indicative of lower regional metamorphic temperatures than are typically assumed.

High fluid pressures decrease the effective stress in a rock unit thereby facilitating faulting (*1*). It has been argued that in order for thrust faulting to occur, P_F must equal P_L (*1*). This concept is consistent with our data in that in the thrust faulted Rocky Mountains, there is good evidence for metamorphic fluids dominating the fluid regime, a situation which is compatible with $P_F = P_L$. However, in the strike-slip and extensional faulted terranes, where the geochemical data indicate that there was significant influx of meteoric water, P_F was most likely substantially less than P_L and hence effective stresses were higher than has been generally assumed.

Quartz ± carbonate veins in the Canadian Cordillera and around the world occasionally host gold mineralization. Most researchers studying these deposits have regarded the deposits as forming from metamorphic fluids (*21, 26*). In the Canadian Cordillera, inclusion fluids from gold-bearing quartz ± carbonate veins consistently have low δD values, indicating that this style of mineralization is a product of the meteoric water convection process. Significant gold mineralization is absent in those areas of the Canadian Cordillera that were dominated by metamorphic fluids (*19*).

The results of this study have significant implications to large-scale crustal processes. The convection of meteoric water in the continental crust should have a significant impact on heat flow and cooling of the crust. In addition, recent suggestions of the interrelations of the hydrosphere and seismic activity have been proposed (*27*). Recognition of the variability in the crustal fluid regime may aid in understanding any linkage between seismic activity and crustal fluids.

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A Rotationally Resolved Fluorescence Excitation Spectrum of *all-trans*-1,4-Diphenyl-1,3-butadiene

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Band 1 in the jet-cooled one-photon $S_1 \leftarrow S_0$ fluorescence excitation spectrum of *all-trans*-1,4-diphenyl-1,3-butadiene has been rotationally resolved with a molecular beam laser spectrometer. Both the orientation of the optical transition moment and the rotational constants of the two vibronic levels have been measured. The molecule shows no evidence of being significantly distorted from a C_{2h} geometry when it is low in the vibrational manifolds of either of the two electronic states.

Few classes of compounds have attracted more attention in the scientific literature than the linear polyenes. From the first demonstration of the

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