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Metamorphic CO_2 degassing from orogenic belts

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Abstract

Kerrick and Caldeira (1993, 1994a) concluded that metamorphic CO_2 degassing in collisional orogens, and especially the Himalayan orogenic belt, could have been an important factor in enhancing paleoatmospheric CO_2 levels and contributing to early Cenozoic global greenhouse warming [Kerrick, D.M., Caldeira, K., 1993. Paleoatmospheric consequences of CO_2 released during early Cenozoic regional metamorphism in the Tethyan orogen. In: Touret, J.L.R., Thompson, A.B. (Guest-Eds.), Fluid–Rock Interaction in the Deeper Continental Lithosphere. Chem. Geol. 108, 201–230.] [Kerrick, D.M., Caldeira, K., 1994a. Metamorphic CO_2 degassing and early Cenozoic paleoclimate. GSA (Geol. Soc. Am.) Today 4, 57–65.]. However, our revised CO_2 mass loss computations for regional metamorphism in the Himalaya–Karakoram belt incorporating recent geochronologic data and revised estimates of the proportion of carbonate source rocks indicate that metamorphic CO_2 degassing from this orogen cannot explain Early Eocene warmth. Widespread pluton-induced hydrothermal flow occurred during the Eocene in the Cordilleran belt of western North America. Synmetamorphic intrusions, which are common in metamorphic belts, may cause significant regional fluid flow. To obtain a representative CO_2 flux from such environments, we computed a CO_2 flux of 1.5×10^{12} mol km^{-2} Ma^{-1} from petrologic and geochemical studies of the Paleozoic plutonic–metamorphic belt in New England (northeastern United States). For the 2×10^6 km^2 area of Eocene metamorphism in the North American Cordillera, the CO_2 fluxes derived from the New England metamorphic belt yield an area-integrated flux of $\sim 3 \times 10^{18}$ mol Ma^{-1}. If a significant fraction of this CO_2 entered the atmosphere, this degassing flux would alone account for Eocene greenhouse global warming. For the Ominica belt within the Cordilleran orogen, a volumetric estimate of the mass of carbonate veins indicates that the consumption of CO_2 by precipitation of carbonate veins may not significantly decrease the amount of CO_2 in fluids that convect to near-surface crustal levels. Compared to other Eocene metamorphic belts, the widespread hydrothermal activity in the North American Cordillera may have been the largest, and most climatically significant, source of metamorphic CO_2 to the Eocene atmosphere. CO_2 degassing by active metamorphism is most significant in extensional regimes of high heat flow. Extensional tectonism and hydrothermal activity in metamorphic belts may have substantially contributed to atmospheric CO_2 content throughout the Phanerozoic. Examples include the Mesozoic circum-Pacific metamorphic belt, and Oligocene–Miocene regional metamorphism in the Himalayan orogen. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Carbon dioxide; Cenozoic; Degassing; Metamorphism; Orogenic belts

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"*The most vexing problem we have encountered in modeling the geochemical carbon cycles is to calculate the rate of degassing of carbon dioxide due to igneous and metamorphic activity.*" R.A. Berner and A.C. Lasaga, 1989

1. Introduction

Modeling the global carbon cycle (Walker et al., 1981; Berner et al., 1983; Kerrick and Caldeira, 1993) shows that on time scales > 1 Ma global temperatures are largely controlled by the relative fluxes of CO_2 consumed by chemical weathering versus CO_2 degassed from metamorphism and magmatism. (Here, we neglect the impact of imbalances in the organic carbon subcycle on atmospheric CO_2 content; Berner et al., 1983.) Our computations (Kerrick and Caldeira, 1993, 1994a) showed that significant greenhouse global warming by Earth degassing would require an additional minimum CO_2 flux of $\sim 10^{18}$ mol Ma^{-1}.

The BLAG and derivative models for the global carbon cycle (Berner et al., 1983; Lasaga et al., 1985; Berner, 1991, 1994) indirectly derived the CO_2 degassing flux. Assuming steady state, the present-day degassing flux was assumed to equal the flux of CO_2 consumed by chemical weathering. A direct estimate of the present-day CO_2 degassing flux is clearly warranted. The CO_2 paleodegassing flux from magmatic and metamorphic sources was linearly related to the rate of sea-floor generation. These contributions recognized the limitations of this correlation; in fact, the original BLAG paper (Berner et al., 1983) ended with a particular appeal for further studies on metamorphic–magmatic CO_2 outgassing. Quantification of CO_2 degassing must consider differences in the nature and extent of metamorphism and magmatism in different tectonic regimes. Correlation of CO_2 degassing with spreading rates neglects differences in metamorphism and magmatism associated with continent–continent and island-arc–continent collision. For example, this correlation would exclude the effects of the widespread regional metamorphism and magmatism following the India–Asia continent–continent collision. Multiple regional metamorphic and magmatic events occurred in the successive docking of island-arc terranes with the North American continent in the Mesozoic and Cenozoic. Furthermore, present-day 'non-volcanic' degassing is concentrated in extensional tectonic regimes (Kerrick et al., 1995) where plate motion is transpressional. Transpressional tectonism would be overlooked in correlating metamorphic and magmatic degassing with spreading rate. Magma generation in subduction zones, and thus the extent of arc magmatism, depends upon the angle of subduction (Wilson, 1989). Analysis of CO_2 emission from present-day volcanism illustrates the problem arising from correlating spreading rates with CO_2 degassing from arc magmatism. In particular, Mt. Etna, which is not in a subduction zone setting, emits far more CO_2 than subduction-related volcanic arcs such as the Andes (Gerlach, 1991; Allard, 1992; Brantley and Koepenick, 1995). Accordingly, to evaluate the correlation between CO_2 degassing and paleoclimate, we focus on the geologic record.

The BLAG and derivative models assumed that CO_2 degassing primarily occurs by arc magmatism associated with subduction zones. In their modeling, Berner and colleagues (Berner et al., 1983; Berner and Lasaga, 1989; Berner, 1991) did not distinguish between two sources of CO_2 in subduction zones: (1) the release of CO_2 by subsolidus metamorphic decarbonation; and (2) magmatic CO_2 degassing. Nevertheless, the cartoon of the global carbon cycle in Berner and Lasaga (1989) implicitly assumed that CO_2 in subducted carbonate would be released by metamorphic degassing at shallower levels or incorporated by anatexis in the production of arc magmatism at greater depths. CO_2 fluxes from subsolidus metamorphic decarbonation may differ greatly from magmatic CO_2 degassing. In the present paper we focus our attention on metamorphic decarbonation.

Kerrick and Caldeira (1993, 1994a) hypothesized that CO_2 released by post-collisional prograde regional metamorphism in the Himalaya–Karakoram orogen may have contributed to Eocene greenhouse global warming. Although our primary focus was on the Himalaya–Karakoram belt, we also considered degassing from the western part of the Tethyan orogenic belt and the circum-Pacific orogenic belts. This paper presents an update of our views in light of new geochronologic studies on the timing of metamorphism, and a field excursion by the authors to the Karakoram–Himalaya of northern Pakistan. Furthermore, we detail herein CO_2 degassing from metamorphism in the Cordilleran belt of western North America, a region that we originally suggested to be an unimportant contributor of metamorphic CO_2 to the Eocene atmosphere (Kerrick and Caldeira, 1993).

2. Reassessment of Eocene metamorphic CO_2 fluxes

2.1. Himalaya–Karakoram orogen

In this section, we review and reassess the hypothesis of Kerrick and Caldeira (1993, 1994a) that metamorphic CO_2 from the Himalaya–Karakoram orogen significantly contributed to Eocene warmth.

In our earlier analysis (Kerrick and Caldeira, 1993, 1994a), we computed the moles (M) of CO_2 released from a given volume (V_{total}) of crust undergoing prograde metamorphism with the equation:

$$M = \frac{V_{total} \times V_F \times \rho \times W_F}{W_{CO_2}}$$

where V_F = vol. fraction of CO_2 source rock, ρ = average rock density (2.7 g cm^{-3}), W_F = wt. fraction of CO_2 released, and W_{CO_2} = molecular weight of CO_2 (44 g mol^{-1}). For carbonate CO_2 source rocks (impure limestones and dolostones), we estimated their proportion at the present level of erosion. The wt.% of CO_2 released from carbonate lithologies was based on the average orogenic carbonate bulk rock composition by Ronov et al. (1990). We also considered pelites as a CO_2 source rock. The average wt.% of CO_2 released in pelitic lithologies was based on estimates of the average CO_2 content of pelitic sediments. Our analysis (Kerrick and Caldeira, 1993) implied that carbonates dominate over organic carbon (e.g., graphite) as a metamorphic CO_2 source.

Our computation of the total volume of crust undergoing metamorphism (Kerrick and Caldeira, 1993, 1994a) was obtained from the total area of exposed metamorphic rocks and estimated depths of the metamorphic orogen. We considered two crustal thicknesses: 30 km (which we considered to be conservative) and 60 km (our preferred value for thickness of the Himalaya–Karakoram metamorphic orogen). Scaling the CO_2 area-integrated flux to the amount released per million years required estimates of the duration of prograde metamorphism, which was constrained by the time between collision and peak metamorphism constrained from geochronologic data. Assuming linear release of CO_2 during the prograde metamorphic event, the area-integrated CO_2 flux was obtained by dividing the total CO_2 released by the estimated duration of prograde metamorphism.

As noted by Kerrick and Caldeira (1993, p. 224), primary uncertainties in our computed area-integrated CO_2 fluxes from the Himalaya–Karakoram orogen involved the timing of prograde metamorphism and the proportion and compositions of CO_2 source rocks. Here we provide an updated analysis in light of these and other uncertainties.

Based on geochronologic data for the timing of metamorphism, Kerrick and Caldeira (1993, 1994a) subdivided the Himalaya–Karakoram orogen into two parts: the central and eastern Himalaya (Garhwal and eastward) versus the western section (the Karakoram and the Himalaya belt in Zanskar and northern Pakistan). The present paper provides a reassessment of metamorphic geochronology in these regions.

2.1.1. Himalaya of India and Tibet

Kerrick and Caldeira (1993) noted that there were no geochronologic data supporting a pre-Oligocene metamorphism from Zanskar eastward (Fig. 1). Nevertheless, some papers (Hodges and Silverberg, 1988; Inger and Harris, 1992) alluded to the possibility that the Miocene metamorphism overprinted an earlier Barrovian-type regional metamorphism. With the uncertainly duly noted (Kerrick and Caldeira, 1993, p. 224), we considered the possibility of Eocene regional metamorphism in the central and eastern part of the Himalayan orogen.

$^{40}Ar/^{39}Ar$ geochronologic data for metamorphic rocks in southern Tibet (Hodges et al., 1994) suggest that there were two periods of metamorphism: an 'Eohimalayan' Late Oligocene event followed by 'Neohimalayan' metamorphism in the Miocene. The study of Hodges et al. (1994) suggests that there was no pre-Oligocene metamorphism in the central Himalaya.

In an analysis of geochronologic data for the Lahul region of the Himalaya in northwestern India,

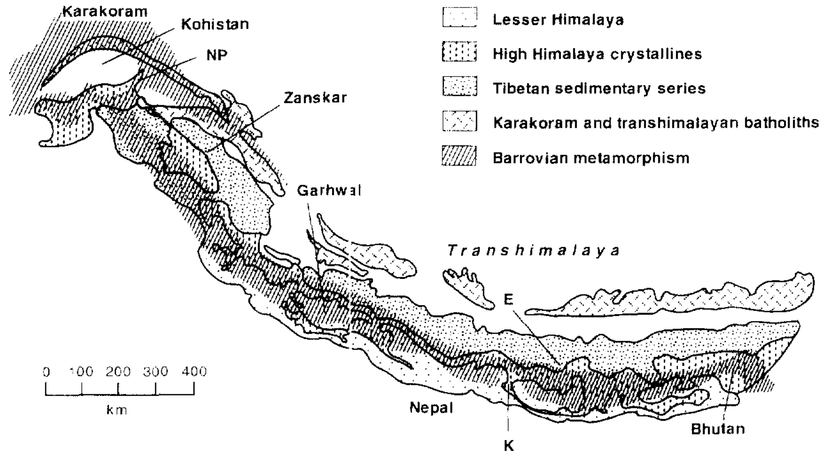

Fig. 1. Map of the Himalayan orogen showing major lithotectonic units (redrawn from Kerrick and Caldeira, 1993, Fig. 5). The shading encompasses rocks affected by Barrovian metamorphism. *E* = Mt. Everest, *K* = Kathmandu, *NP* = Nanga Parbat. See Kerrick and Caldeira (1994a, Fig. 2) for the location of this area in southeastern Asia.

Vannay and Steck (1995) concluded that peak metamorphism occurred at 40–30 Ma. In the Kashmir–Zanskar region of northwestern India, peak metamorphism occurred at 20–30 Ma (Searle, 1996). To correlate with the Late Paleocene–Early Eocene period of global warming, prograde metamorphism at 55–50 Ma is required (Kerrick and Caldeira, 1993); thus, prograde metamorphism in the Lahul region apparently post-dated this time period. In contrast to our previous papers (Kerrick and Caldeira, 1993, 1994a), we now consider that the Higher Himalayan Crystalline Series of northwestern India (Zanskar–Ladakh–Lahul) did not undergo Eocene metamorphism; consequently, our original estimate of the amount of metamorphic CO_2 production in the northwestern part of the Himalayan belt must be reduced by the omission of this ~300-km-long section of the Himalayan belt.

In light of recent geochronologic data we conclude that regional metamorphism of the Himalaya from northwest India (Lahul, Ladakh, Zanskar) and eastward post-dated the Late Paleocene–Early Eocene global warming. Metamorphism may have been diachronous, with earlier metamorphism occurring in the northwestern India Himalaya and later metamorphism in the central Himalaya (Nepal) (Guillot et al., 1996; Searle, 1996). This diachroneity is compatible with a counterclockwise pivoting of the Indian plate (and progressive eastward suturing) during collision with the Asian plate.

Searle (1996) concluded that the India–Asia collision in the section from Ladakh to southern Tibet occurred at about 50 Ma. If regional metamorphism required a minimum of ~10 Ma following collision (Kerrick and Caldeira, 1993, 1994a), the earliest metamorphism would have occurred at ~40 Ma. Indeed, the Oligocene metamorphism in the central Himalaya is compatible with regional metamorphism beginning no earlier than ~40 Ma.

2.1.2. Northern Pakistan

Barring evidence for Eocene metamorphism in the Himalayan belt of India and Nepal, we conclude that Eocene prograde metamorphic CO_2 production in the Himalayan orogenic belt was confined to the Pakistan Himalaya and Karakoram.

In the Himalaya of Pakistan, metacarbonate rocks primarily occur in the Higher Himalayan Crystalline Series south of the Kohistan Arc (Fig. 2). The metacarbonates were originally Indian shelf sediments deposited on metamorphic basement.

Calcareous rocks are abundant in Paleozoic and Mesozoic metasedimentary units of the Higher Himalayan Crystalline Sequence of the Pakistan Himalaya (Fig. 2). The total exposed area of these units (Fig. 2) is ~6000 km^2. Assuming that the metamor-

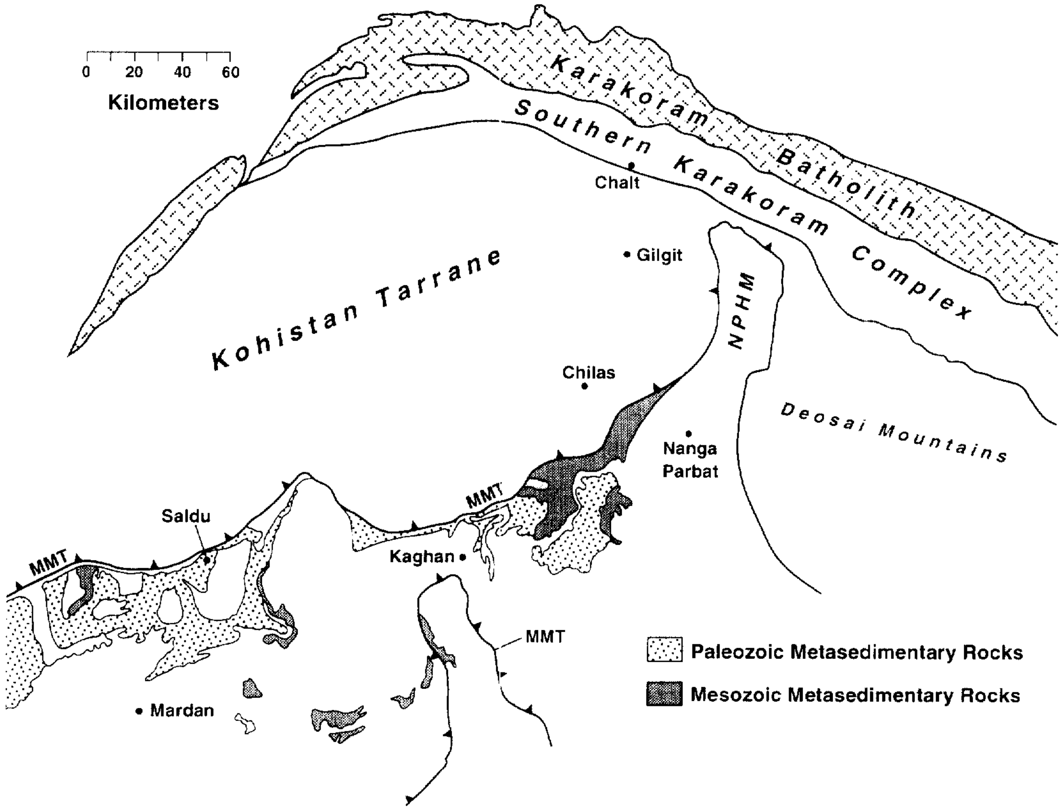

Fig. 2. Geologic map of northern Pakistan (from Searle and Khan, 1996). See Fig. 1 for location of this area within the Himalayan belt. Pertinent to the present study are metasedimentary rocks of the Higher Himalayan Crystalline Series and the Southern Karakoram Complex. *MMT* = Main Mantle Thrust. *NPHM* = Nanga Parbat Haramosh Massif.

phic sequence extended to depths of 30 km, and with a liberal estimate of 10 wt.% CO_2 evolved during metamorphism (Kerrick and Caldeira, 1993), $\sim 10^{18}$ mol of CO_2 would have been evolved. Assuming prograde metamorphism took 10 Ma (Kerrick and Caldeira, 1993), the area-integrated flux of CO_2 would be $\sim 10^{17}$ mol Ma^{-1}. As noted by Kerrick and Caldeira (1993, 1994a) not all of the CO_2 generated at depth would have escaped to the surface. Moreover, non-calcareous rocks are common in the Higher Himalayan Crystalline Sequence. In the Swat region (near Saidu in Fig. 2) carbonate rocks primarily occur in the Kushala Formation, which constitutes less than half of the total metasedimentary stratigraphic sequence (DiPietro et al., 1993). Because significant global warming requires area-integrated fluxes $> 10^{18}$ mol Ma^{-1} (Kerrick and Caldeira, 1993), our revised mass loss calculations suggest that metamorphic CO_2 degassing of carbonate rocks during the Eocene metamorphism of the Higher Himalayan Crystalline Sequence in northern Pakistan cannot explain Eocene warmth.

In the Karakoram the primary carbonate unit is the Dumordu marble, a unit within the Southern Karakoram Metamorphic Complex (Fig. 2). The Dumordu marble is several kilometers in structural thickness and has a strike length of ~ 300 km. The authors examined and sampled the ~ 6 km section of the Dumordu marble exposed in the Hunza Valley. Aside from a few interlayers of siliceous rocks, the Dumordu marble appears to be very constant in modal mineralogy. Carbonate constitutes at least 95% by volume of the rock, and the primary impurity is phlogopite. To compute the CO_2 released during phlogopite formation, we assume that the Dumordu marble averages 5 vol.% phlogopite, and consider that a primary phlogopite-producing reaction in impure dolomites is (Bucher and Frey, 1994):

K-feldspar + 3 Dolomite + H_2O

= Phlogopite + 3 Calcite + 3 CO_2

With outcrop dimensions of 5 km × 300 km, and an assumed crustal thickness of 30 km, the total CO_2 loss would be 4.5×10^{16} mol. Assuming prograde metamorphism took 10 Ma (Kerrick and Caldeira, 1993) the rate of CO_2 loss would be 4.5×10^{15} mol Ma^{-1}.

Based on mass loss computations we conclude that CO_2 degassing during Paleocene and Eocene metamorphism in northern Pakistan and the Karakoram was considerably less than needed to produce significant global greenhouse warming (i.e., $\geq 10^{18}$ mol Ma^{-1}).

2.1.3. Uncertainty in mass loss computations

As noted by Kerrick and Caldeira (1993, p. 224), our method of computing metamorphic CO_2 fluxes from decarbonation mass loss is subject to number of potentially large sources of error. A major uncertainty stems from limited information on bulk rock compositions, modal mineralogy, and, hence, uncertainty in computing an integrated metamorphic CO_2 loss for a large metamorphic belt. There is uncertainty in estimating proportions of metamorphic rocks from the present level of exposure, and assuming that these proportions are analogous to the eroded and subsurface metamorphic rocks of this orogen.

2.1.4. Analysis of Goddéris and François (1995)

Using an energy balance climate model, Goddéris and François (1995) analyzed and interpreted the Mesozoic and Cenozoic variations in the $^{87}Sr/^{86}Sr$ isotopic ratio of seawater. They focused on the role of the Himalayan orogen on Cenozoic paleoclimate. Following Kerrick and Caldeira (1993) their model of the global carbon cycle incorporated the effect of metamorphic CO_2 degassing in the Himalayan orogen. They noted that with the India–Asia collision at 50 Ma, post-collisional metamorphism would have post-dated the period of Early Eocene global warming. Thus, they concluded that "*... the degassing event did not occur, at least not with such magnitude*" (Goddéris and François, 1995, p. 186). Their analysis overlooked the Late Paleocene–Early Eocene regional metamorphism in the northern Pakistan Himalaya and Karakoram, which Kerrick and Caldeira (1993) concluded could have contributed significant CO_2 to Eocene atmosphere. Nevertheless, our reassessment of Eocene metamorphic CO_2 degassing from this area supports the contention of Goddéris and François (1995) that in the early Cenozoic, metamorphic CO_2 degassing in the Himalayan orogenic belt may have had a far more insignificant effect on the global climate than suggested by Kerrick and Caldeira (1993).

2.1.5. Bickle's (1996) analysis

Bickle (1996) argued that episodicity in the $^{87}Sr/^{86}Sr$ seawater curve implies a corresponding cyclicity in tectonism, metamorphism and global weathering rate. In analyzing the role of metamorphic CO_2 degassing on Cenozoic paleoclimate, he stressed the marked increase in the seawater $^{87}Sr/^{86}Sr$ beginning at 40 Ma. Bickle (1996) attributed this increase to enhanced chemical weathering due to uplift of the Himalayan orogen, and concluded that CO_2 degassing from this orogen supplied atmospheric CO_2 that was consumed by chemical weathering. Estimating the volume of metamorphic rock removed by erosion in the Himalayan system ($\sim 5 \times 10^7$ km^3), and an arbitrary average carbonate content of 5 wt.% in the protolith, Bickle (1996) computed a total CO_2 release of $\sim 6 \times 10^{19}$ mol. He derived a total CO_2 loss of 2.4×10^{19} mol from an average value of time-integrated metamorphic fluid fluxes, an estimated fluid composition of $X_{CO_2} = 0.10$, and assuming fluid flow through 10 km of crust. Accordingly, using two independent computational strategies, Bickle (1996) implied that his computed amount of CO_2 released from Himalayan metamorphism ($> 10^{19}$ mol) was adequate to account for the atmospheric CO_2 consumed by chemical weathering of the Himalayan belt. Bickle's (1996) analysis implied that metamorphism and unroofing commenced in the Middle Eocene. However, we are not aware of any data substantiating this contention. Harris (1995) used the seawater $^{87}Sr/^{86}Sr$ curve to argue for rapid, synchronous cooling and unroofing of the Himalaya in the Early Miocene (15–20 Ma). For the central and eastern Himalaya, which are considered to have undergone metamorphism in the

Late Oligocene and Miocene (see Section 2.1.1), Kerrick and Caldeira (1993) computed a total CO_2 release of $4–8 \times 10^{18}$ mol. Global warming induced by metamorphic CO_2 degassing in the Late Oligocene and Miocene would have required efficient expulsion of the CO_2 to the Earth's surface and relatively rapid prograde metamorphism (i.e., a few million years). If prograde metamorphism required a minimum of 10 Ma (Kerrick and Caldeira, 1993), our computed amount of CO_2 released by metamorphism in the central and eastern Himalaya would be less than 10^{18} mol Ma^{-1} and, thus, insufficient to cause global warming. Bickle's (1996) larger estimate of total metamorphic CO_2 loss ($> 10^{19}$ mol) implies a potentially significant role of Himalayan CO_2 degassing on paleoclimate. However, we consider his assumption of an average carbonate content of 5 wt.% in the protolith of the sediment eroded from the Himalayan belt to be excessive in that a significant fraction of the exposed metamorphic rocks in the central and eastern Himalaya were probably derived from protoliths with little or no carbonate. We estimate (Kerrick and Caldeira, 1993, p. 219) that carbonate-bearing protoliths probably do not exceed 25% of the Higher Himalayan Crystalline Series. While there is uncertainty in using the present level of exposure to provide an estimate of the bulk composition of the rocks that underwent metamorphism (cf. Bickle, 1996, p. 273), the present level of exposure provides an important constraint on the estimate of the abundance of carbonate in the Higher Himalayan Crystalline Series. Because of significant differences in the lithologies in different metamorphic belts (Yardley, 1997), arbitrary assumptions about the proportions of CO_2 source rocks are not advised (cf. Bickle, 1996).

2.2. *Cordilleran orogen*

Following a brief analysis of the extent of Cenozoic metamorphism in the circum-Pacific orogenic belt, Kerrick and Caldeira (1993) concluded that most of the metamorphic CO_2 in the Paleocene–Eocene was produced from the Tethyan belt. However, in Kerrick and Caldeira (1994a), we noted that the Eocene metamorphic belt in western North America may considerably exceed the size of the Eocene metamorphic belt in the Himalaya–Karakoram. In a subsequent study involving the senior author (Nesbitt et al., 1995), it was concluded that during the Eocene there was widespread metamorphic CO_2 degassing in the North American Cordillera.

In the Mesozoic, the Cordilleran belt in western North America underwent widespread thrusting, folding, metamorphism and intrusion in a compressional tectonic regime. Due to changes in relative plate motion, a marked shift from compression to extension occurred at 60–55 Ma, which resulted in extensional faulting, magmatism and widespread development of metamorphic core complexes (Bardoux and Mareschal, 1994). Margaritz and Taylor (1986) showed a remarkably consistent west-to-east asymmetry in the δD values of plutonic rocks in the 3000-km-long magmatic belt of the Cordillera. This provides primary support for their conclusion that there was "... *intense meteoric-hydrothermal alteration during a very widespread Eocene plutonic-volcanic event* ..." (Margaritz and Taylor, 1986, p. 2215). In the Ominica belt of British Columbia, extensive hydrothermal activity during this extensional event is evidenced by abundant quartz–carbonate veins (Nesbitt et al., 1995). Eocene cooling ages of biotite and muscovite in the southern Ominica belt (Parrish et al., 1988) suggest that post-metamorphic thermal re-equilibration occurred in the Eocene.

For the Cordilleran hydrothermal activity at 60–55 Ma, Nesbitt et al. (1995) used a simplified convection model to estimate the amount of CO_2 transported to the Earth's surface. They postulated that CO_2 was released by metamorphic decarbonation caused by deep infiltration of meteoric water. Their modeling yielded a volumetric advective flux of aqueous fluid ($\sim 10^{-3}$ m^3 m^{-2} a^{-1}). A CO_2 flux (3.8×10^{12} mol km^{-2} Ma^{-1}) was derived by coupling the aqueous fluid flux with data on CO_2 contents of fluid inclusions in quartz veins formed during the hydrothermal event. Nesbitt et al. (1995) alluded to the widespread Eocene intrusions in this region as a heat source for hydrothermal convection. For the entire area covered by Eocene extension and igneous activity in western North America ($\sim 2 \times 10^6$ km^2), as shown in Fig. 3, Nesbitt et al. (1995) computed an area-integrated CO_2 flux of $1.5–7.6 \times 10^{18}$ mol Ma^{-1}. Nesbitt et al. (1995) concluded that

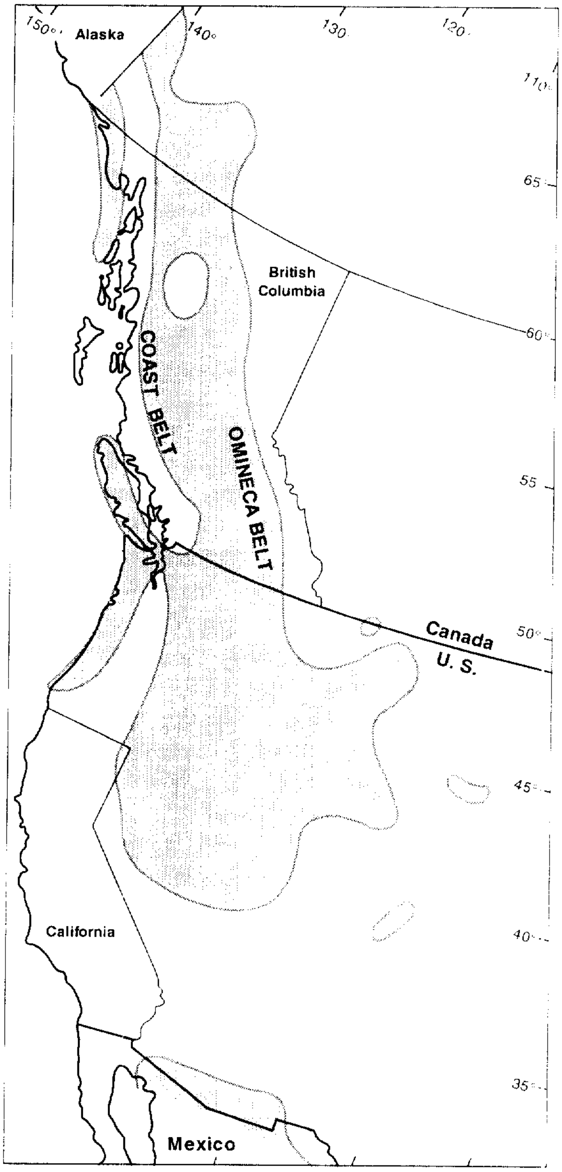

Fig. 3. Magmatic belt (shaded) for the time interval 40–55 Ma in the North American Cordillera. Redrawn from Armstrong and Ward (1991, Fig. 2).

this CO_2 flux would have substantially contributed to Eocene atmospheric CO_2 contents, and thus, to Eocene global warming. According to Kerrick and Caldeira, an additional area-integrated CO_2 flux of $1.5–7.6 \times 10^{18}$ mol Ma^{-1} would produce an average global temperature increase ranging from 3°C to 8°C. Barron (1987) estimates that the Eocene global mean temperature was about 2°C warmer than at present. Barron's estimate could be somewhat low, if tropical sea-surface temperatures were warmer than previously believed (Zachos et al., 1994). Thus, the lower range of the area-integrated CO_2 flux computed by Nesbitt et al. (i.e., $\sim 2 \times 10^{18}$ mol Ma^{-1}) is compatible with estimates of Eocene paleotemperatures.

Considerable documentation of quartz–carbonate veins formed during the Eocene hydrothermal event in the Cordilleran orogen has been recently published (Nesbitt and Muehlenbachs, 1995a,b; Nesbitt, 1995). The veins are most abundant in low-grade metamorphic rocks (greenschist facies or lower grade). Correlation of vein mineralogy with metamorphic grade provides cogent evidence that vein formation was associated with the metamorphic event (Nesbitt and Muehlenbachs, 1995b). However, the veins apparently post-dated the peak of metamorphism (Nesbitt, 1995). Nesbitt and Muehlenbachs (1995b) attributed the marked homogeneity of $\delta^{18}O$ values of vein-forming fluids over a large section of crust to interaction of deeply circulating meteoric water with rocks at temperatures exceeding 350°C. A generalized model for vein formation in the Cordillera is extensional tectonism and magma-induced fluid convection through fractured crust (Nesbitt, 1995) and contemporaneous erosional uplift leading to unroofing of metamorphic core complexes (Parrish et al., 1988). Nesbitt and Muehlenbachs (1995b) concluded that convective circulation was largely confined to depths shallower than the brittle–ductile transition ($\sim$ 10 km).

Evidence supporting widespread hydrothermal activity related to intrusive magmatism was presented by Ward (1995). His compilation of radiometric age dates for porphyry copper deposits in western North America (Ward, 1995, Fig. 1D) shows a marked abundance at 60–50 Ma. Geographically, Eocene porphyry copper deposits are abundant in two 1700-km-long segments of the Cordilleran belt: one between Guadalajara, Mexico, and Los Angeles, California, and the other extending from southern British Columbia to Alaska (Ward, 1995, Fig. 2).

Ward's (1995) compilation reveals three major 'subduction cycles' in western North America during the Mesozoic and Cenozoic. Each cycle began with trench-normal contraction, rapid subduction and widespread andesitic magmatism, followed by a period of trench-normal extension, widespread silicic magmatic activity, rifting and terrane rotation, mylonitization of metamorphic core complexes and extensive fluid circulation. Rapid subduction occurred at 140–120 Ma and 87–36 Ma, and more moderate subduction occurred at 140–120 Ma. In addition to abundant porphyry copper deposits associated with the latest period of rapid subduction (87–36 Ma), porphyry copper deposits correlative with the earliest subduction period (140–120 Ma) were documented by Ward (1995).

The map of Armstrong and Ward (1991) showing the total area of magmatic activity during 40–55 Ma in western North America (covering a total area of $\sim 2 \times 10^6$ km^2) was used by Nesbitt et al. (1995) to compute an area-integrated CO_2 flux of ~ 1.5–7.6×10^{18} mol Ma^{-1}. Excluded in this computation was Eocene magmatism in the southwestern United States and Mexico. Evidence for widespread hydrothermal activity in southwestern North America is a large area containing Eocene porphyry copper deposits in this region (Ward, 1995, Fig. 10). A convective CO_2 flux of 3.8×10^{12} mol km^{-2} Ma^{-1} calculated by Nesbitt et al. (1995) yields an area-integrated CO_2 flux of $\sim 2.6 \times 10^{18}$ mol Ma^{-1} for the $\sim 6.8 \times 10^5$ km^2 area of Eocene hydrothermal activity shown on Ward's (1995, Fig. 10) map of the southwestern U.S. and northwestern Mexico.

Erdmer and Mortensen (1993) described a 1200-km-long Eocene metamorphic–plutonic belt extending for about 1200 km northwestward from 55°N. The plutonic belt shown in Erdmer and Mortensen (1993) overlaps the northern portion of the Eocene intrusive belt of Armstrong and Ward (1991). As with the southern Ominica belt in British Columbia, the spatial and temporal correlation of plutonic and metamorphic rocks in this belt suggest the importance of intrusives as a heat source for the metamorphism. In southwestern Yukon, radiometric dating shows that the peak of metamorphism and intrusion occurred at 56–58 Ma, and cooling and unroofing occurred at ~ 55–39 Ma (Erdmer and Mortensen, 1993). This timing scenario is similar to that of the southern Ominica belt, thus arguing for a model of uplift and extension which may have promoted convective circulation of meteoric waters and infiltration-driven decarbonation. Support for this interpretation comes from the 200-km-long Juneau gold belt characterized by mesothermal gold-bearing quartz vein deposits (Goldfarb et al., 1988, 1991). Radiometric ages for these veins cluster within a very narrow time period (55–56 Ma), thus arguing for a major hydrothermal event in the Early Eocene. Goldfarb et al. (1991) concluded that the vein-forming fluids, generated during an earlier metamorphic event, were trapped at depth because of low permeabilities accompanying convergent tectonism in the overlying crustal wedge. Subsequently, a shift to transpressional tectonism provided the necessary fracture and fault network for fluid escape to shallower crustal levels. However, as in the model for the Ominica belt, it is alternatively possible that Eocene transpressional tectonism allowed deep convective circulation of meteoric waters. Intrusives below the level of exposure of the veins could have provided a heat source. The lack of nearby intrusives of Eocene age at the present level of exposure does not necessarily preclude their presence at depth.

West of the Ominica belt is the Coast belt, consisting of abundant Mesozoic and Cenozoic intrusives. Metamorphism in this region appears to have been affected by regional thermal gradients and is thus more akin to low-pressure regional metamorphism than contact metamorphism (Woodsworth, 1979; Kerrick and Woodsworth, 1989; Greenwood et al., 1991). Thermobarometry and geochronologic data suggest that the high-grade part of the Coast belt experienced rapid uplift and cooling in the early Cenozoic. Greenwood et al. (1991) suggested that this uplift occurred by extensional tectonism. Accordingly, we consider that regional-scale infiltration-driven devolatilization to be likely during the Eocene extensional event in the Coast belt.

Nesbitt et al. (1995) confined their analysis of Eocene metamorphism to the Cordilleran belt southeast of the Yukon–Alaska border (Fig. 3). However, a 1600-km-long belt of rocks with an Eocene metamorphic overprint occupies most of southern Alaska (Dusel-Bacon, 1994). Dusel-Bacon (1994) noted that the Eocene metamorphism occurred under relatively low pressures and was accompanied by widespread intrusion of plutons. Evidence of extensive fluid transport (Sission and Hollister, 1988; Sission et al.,

1989) supports the possibility of widespread infiltration driven by plutonic heat. Regardless of the tectonic regime, inclusion of the Eocene metamorphic belt in Alaska suggests that the Eocene metamorphic–plutonic belt in western North America is the world's largest contiguous belt of this age and type. Accordingly, from a worldwide perspective, we suggest that the Cordilleran belt is the most likely orogen to have released climatically significant quantities of metamorphic CO_2 in the early Cenozoic.

3. Metamorphic CO_2 fluxes during Paleozoic regional metamorphism in New England

The methodology of Nesbitt et al. (1995) is attractive because the hydrothermal fluid compositions are directly determined by fluid inclusions. The relative constancy of the fluid inclusion compositions in veins throughout the southern Canadian Cordilleran metamorphic belt is particularly advantageous for computing large-scale fluid fluxes. However, the computations of Nesbitt et al. (1995) where made by modeling the upper 10 km of crust with homogeneous permeability and a homogeneous subjacent heat source. Geologic evidence suggests that in regional metamorphic regimes with synmetamorphic plutons as major heat sources, such as the southern Ominica belt, fluid flow is heterogeneous. Probably the best studied example of pluton-induced infiltration-driven metamorphism is the regionally metamorphosed rocks in New England. To obtain a representative CO_2 flux from such metamorphic environments, we computed CO_2 fluxes from petrologic and geochemical studies of the New England Paleozoic plutonic–metamorphic belt.

Regionally metamorphosed rocks in south-central Maine and eastern Vermont appear to delineate giant metamorphic hydrothermal plumes that are centered around synmetamorphic granitic intrusions (Ferry, 1994). As such, these areas serve as excellent case studies for evaluating the heterogeneity of pluton-driven fluid flow. Ferry (1992) and Léger and Ferry (1993) contend that the fluids flowed horizontally toward the intrusions and that focused upward flow occurs in the vicinity of the intrusives. Ferry (1992) concluded that the size and fluid flow geometry of the regional metamorphic hydrothermal systems of eastern Vermont were similar to that of mid-ocean ridge hydrothermal systems.

Extensive petrographic investigations of reaction progress, coupled with a mass-conservation equation, have delineated time-integrated fluid fluxes in regionally metamorphosed rocks in eastern Vermont (Ferry, 1992; Léger and Ferry, 1993). The estimated fluxes increase with increasing metamorphic grade, in part a reflection of the increase in internally generated volatiles with increasing grade (Ferry, 1992). The spatial correlation of the zones of highest fluxes with intrusives (see Léger and Ferry, 1993, Fig. 5), and the presence of abundant quartz veins, suggest that these zones may have experienced significant upward fluid flow. Taking the estimates by Léger and Ferry (1993) of the average time-integrated fluid flux ($\sim 10^5$ cm^3/cm^2) and average X_{CO_2} (0.45), the average time-integrated upward CO_2 flux would be $\sim 1.5 \times 10^{13}$ mol km^{-2}. The duration of metamorphism is poorly constrained; however, here we follow Léger and Ferry (1993, p. 20) and equate the estimate by Christensen et al. (1989) of ~ 10 Ma for the duration of growth of garnet porphyroblasts to the duration of the hydrothermal event. Accordingly, the average upward CO_2 fluxes during prograde metamorphism in eastern Vermont would have been $\sim 1.5 \times 10^{12}$ mol km^{-2} Ma^{-1}.

Léger and Ferry (1993) estimated a pressure of ~ 4.5 kbar for regional metamorphism in eastern Vermont. Because Léger and Ferry (1993) considered it unlikely that meteoric water infiltrates to the implied depths (15 km), they considered hydrous granitic magma to be the probable source of fluids. From estimates of the solubility of water in granitic melts, Léger and Ferry (1993) determined that the amount of magmatic water needed for the high-grade zones of upward flow adjacent to intrusives was insufficient and thus appealed to an additional source for water. Fluid flow in the eastern Vermont regional metamorphism requires a recharge source away from the intrusives. Léger and Ferry's (1993) rejection of penetration of meteoric water to mid-crustal levels may be questioned in light of the isotopic study by Wickham and Taylor (1985), suggesting that meteoric waters penetrated to depths of ~ 12 km during metamorphism in the Trois Seigneurs Massif of the French Pyrenees. However, as summarized in the next section, we consider widespread convection of meteoric water to such mid-crustal levels to be unlikely. Accordingly, further research is required on the source of fluids that recharged deep hydrothermal systems such as the Trois Seigneurs Massif and the metamorphic belt in New England.

4. Present-day metamorphic CO_2 degassing

In addition to CO_2 discharged from the craters and flanks of volcanoes, considerable CO_2 emission is occurring by convective hydrothermal circulation in high heat flow regions (Kerrick et al., 1995). Kerrick et al. (1995) argued that the integrated global flux of CO_2 from such regions could be equivalent to the CO_2 flux from active volcanoes. Analysis of the 'non-volcanic' CO_2 emission is useful to evaluate the source of CO_2 and the geologic–tectonic settings where large CO_2 fluxes occur. The principle of uniformitarianism allows us to use present-day metamorphic and volcanic degassing to gain insight into the geologic–tectonic regimes in which degassing may have been significant in the past.

Kerrick et al. (1995) showed that elevated regional CO_2 fluxes occur in high heat flow regions experiencing extensional tectonism. Notable examples include the Taupo Volcanic Zone, New Zealand, the Salton Trough in southwestern North America, the north-central Coast Range in western California, and central Italy. Gas chemistry and geologic setting suggest a diverse origin for the CO_2. In the Taupo Volcanic Zone, the dominant CO_2 source appears to be subjacent intrusives (Kerrick et al., 1995; Seward and Kerrick, 1996). This is compatible with the occurrence of the Taupo Volcanic Zone in a back-arc basin. In contrast, CO_2 emanating from the Salton Trough is dominantly produced by metamorphic decarbonation (Kerrick et al., 1995). However, the Salton Trough presents a relatively unique setting in that active metamorphism is occurring in a large depositional trough formed by the landward extension of a mid-ocean ridge (the East Pacific Rise).

Compared to the Salton Trough, CO_2 degassing in central Italy may provide a more typical modern analog for pluton-driven metamorphic CO_2 degassing in an extensional setting. In a recent summary of CO_2 degassing in central Italy, Chiodini et al. (1995) concluded that the CO_2 is primarily produced from metamorphic decarbonation of marine carbonate rocks. In addition to carbon isotopic data, their conclusion is supported by geophysical evidence of subsurface carbonate rocks. Widespread Quaternary volcanism of the alkaline-potassic Roman Comagmatic Province, coupled with elevated heat flow, is compatible with a magmatic heat source. Central Italy is presently undergoing transpressional tectonism, thereby providing a fault and fracture network for escape of gas to the surface. The isotopic signatures of the thermal waters associated with the CO_2 springs in central Italy suggest a meteoric source. Accordingly, metamorphic decarbonation induced by deep infiltration of meteoric water is reasonable for this region. Chiodini (1994) and Chiodini et al. (1995) concluded that the redox state of the gas was produced by reaction and equilibration with the permeable carbonate rocks into which the gas percolated from depth. Accordingly, they suggested that the gases were trapped in permeable limestone aquifers overlain by impermeable aquitards and subsequently expelled through faults and fractures in the overlying aquitards. A similar mechanism (i.e., storage of CO_2 in reservoirs at depth) was proposed for CO_2 emanating from southeastern France (Arthaud et al., 1994). As such, this supports the hypothesis of Goldfarb et al. (1991) who contend that quartz veins of the Juneau gold belt in southeastern Alaska formed from the release via tectonic activity of volatiles that were generated by an earlier regional metamorphism and stored in reservoirs. G. Chiodini and colleagues (G. Chiodini, pers. commun.) have measured a CO_2 flux corresponding to 1.7×10^9 mol a^{-1} from a 0.4 km^2 area of focused CO_2 emission at Poggio Olivo (locality given in Chiodini et al., 1995). As there are numerous other areas of focused CO_2 emission in this region (Chiodini et al., 1995, Table 1), it is likely that the area-integrated CO_2 flux in central Italy considerably exceeds the 10^{10} mol a^{-1} estimate of Kerrick et al. (1995). Chiodini et al. (1995) contend that in central Italy much of the CO_2 reaching the Earth's surface is dissolved in groundwater. Hence, significant quantities of CO_2 could also be released to the atmosphere by diffuse emission. Results of preliminary research of the senior author and colleagues on central Italy CO_2 degassing is summarized in Rogie et al. (1996). The CO_2 flux from focused degassing in central Italy may considerably exceed that of the entire Taupo Volcanic Zone (estimated at 10^{10} mol a^{-1} by Seward and Kerrick, 1996).

In the areas of high CO_2 fluxes considered by Kerrick et al. (1995), fluid flow occurs by convection of meteoric water driven by heat from subjacent intrusives. However, in areas of high relief, topographically driven fluid flow is important. In such cases, the hydrostatic pressure head drives fluid flow from higher to lower elevations. Notable examples are the New Zealand Alps (Jenkin et al., 1994; Upton et al., 1995), the Nanga Parbat Massif in northern Pakistan (Craw et al., 1994), and the Main Central Thrust in Nepal (Marty et al., 1996). Fluid flow is evidenced by thermal springs and veins.

In the New Zealand Alps, the isotopic composition of water in fluid inclusions of quartz veins, and the isotopic composition of water emanating from thermal springs, matches that of meteoric water (Jenkin et al., 1994). In addition, the $\delta^{18}O$ of vein quartz is indicative of precipitation from a fluid with water of meteoric origin (Upton et al., 1995). Fluid inclusions have significant quantities of CO_2 (15–20 mol%). From carbon isotopic data on fluid inclusions and warm springs, Jenkin et al. (1994) suggested that CO_2 may be produced from the oxidation of graphite rather than metamorphic decarbonation of calcite. Regardless of the source, the evidence suggests that CO_2 is produced by fluid–rock reaction associated with the infiltration of meteoric water into steeply dipping fissures. Microthermometry suggests that the veins formed over a temperature range of 200–350°C and depths up to 6 km. This illustrates that meteoric water can penetrate to, or perhaps through, the brittle–ductile transition (Jenkin et al., 1994; Upton et al., 1995).

Contemporary topographically driven hydrothermal fluid flow analogous to that of the New Zealand Alps is occurring in the Nanga Parbat Massif of northern Pakistan (Craw et al., 1994). Microthermometry of fluid inclusions in quartz veins that formed from this hydrothermal activity suggests that fluids of meteoric origin penetrated to the vicinity of the brittle–ductile transition (6 km depth and temperatures above 400°C). The origin of CO_2 present in the fluid inclusions was not discussed by Craw et al. (1994). However, thin carbonate-bearing interlayers are common in the pelitic schists of the Nanga Parbat Massif (Misch, 1964); thus, infiltrating meteoric waters could induce metamorphic decarbonation (or calcite dissolution) at depth.

Contemporary topographically driven fluid flow may drive fluid flow in CO_2 thermal springs of central Italy. The geographic location of the springs, chemistry of the groundwater, and regional hydrology suggest that the waters exiting from the thermal springs originated as rainwater in the Apennines to the east (Minissale, 1991; Minissale et al., 1997), flowed through a permeable carbonate aquifer and acquired CO_2 influxed from depth, and exit to the surface through permeable structures (faults) in the western part of the Italian Peninsula. The thermal springs precipitate large quantities of travertine and, thus, degass CO_2 to the atmosphere by the carbonate-precipitating reaction. The large number of thermal springs in central Italy, and associated travertine deposits, could provide a significant CO_2 flux to the atmosphere.

Considerable CO_2 degassing is occurring in the north-central Coast Ranges of California (Kerrick et al., 1995). As with other areas of high heat flow and extensional tectonism, isotopic data suggest that the water has a meteoric origin. Based on the chemistry and isotopic compositions of the gases, the CO_2 appears to have a significant organic signature perhaps arising from the decomposition of organic material by active metamorphism at depth. Modeling of heat flow anomalies (Liu and Furlong, 1992) suggests that significant quantities of basaltic magma may be stored in the deep crust ($\sim$ 30 km depth), thus providing a heat source for widespread active metamorphism of the basement (Franciscan Formation) at depth. CO_2 vents along the Bartlett Springs fault zone provide evidence of expulsion along fault zones. Most of the earthquakes along the Bartlett Springs fault zone occur at depths of 6–12 km (Dehlinger and Bolt, 1984), thereby indicating that brittle behavior extends to appreciable depths. However, in the Geysers Geothermal field, most of the steam is extracted from depths up to 6 km (Oppenheimer, 1986). As the top of the large subjacent magma chamber is at a depth of about 7 km (Stanley and Blakely, 1995), the Geysers Geothermal field provides an example of intrusive-driven convective flow of meteoric water. Because most of the earthquakes along the nearby San Andreas fault occur at depths less than about 7 km (Miller and Furlong, 1988), we suggest that widespread circulation of meteoric water in this region occurs to maximum depths of ~7 km. This geophysical evidence is compatible with the consensus that the flow of groundwater is restricted to maximum depths of ~6 km (Person and Baumgartner, 1995).

5. Discussion

5.1. Shallow crustal degassing

Studies of active metamorphic CO_2 degassing suggest that the volatiles are generated at relatively shallow crustal levels. Infiltration of meteoric waters to the vicinity of the brittle–ductile transformation may generate much of the metamorphic CO_2 that is escaping to the Earth's surface. In high heat flow regimes, the brittle–ductile transformation occurs at depths of ~6 km and corresponding temperatures of ~350–400°C. CO_2 springs of non-volcanic origin occur in areas of high heat flow and extensional tectonism. Thus, magma-induced hydrothermal circulation of meteoric waters in highly permeable crust would provide an effective mechanism for infiltration-driven, low-grade decarbonation. The studies by Ferry (1994) show that extensive decarbonation occurs in marls subjected to temperatures of ~400°C, so that widespread decarbonation is predicted for fluid infiltration to temperatures of the brittle–ductile transition.

Pervasive decarbonation in the Paleozoic metamorphism in New England occurred at depths of 10–15 km. With the exception of the suggestion by Wickham and Taylor (1985, 1990) of widespread infiltration of meteoric water to depths of ~12 km during metamorphism in the Trois Seigneurs Massif in the Pyrenees, it is unlikely that widespread convective circulation of meteoric water occurs at depths exceeding 10 km (Fournier, 1991). Indeed, from analysis of contact metamorphism of the Sierra Nevada, widespread convection of meteoric water may have been confined to maximum depths of ~8 km (Hanson et al., 1993).

Deep circulation of meteoric water requires maintenance of a hydrostatic head. However, in central Italy there is evidence for storage of highly pressurized CO_2 in reservoirs. Accordingly, a model of continuous metamorphic decarbonation induced by steady-state convection of meteoric water may be inapplicable to central Italy. In seismically active areas, such as central Italy, we envision that through time the flux of CO_2 to the Earth's surface may vary considerably. Periods of seismicity may induce fracture permeability and thus promote elevated fluxes of CO_2. Accordingly, release of CO_2 from gas reservoirs would be controlled by seismicity.

5.2. Deep crustal degassing

In Kerrick and Caldeira (1993, 1994a), we considered CO_2 degassing produced by prograde metamorphism arising from thermal relaxation of the crust upon tectonic thickening due to collision. Metamorphic rocks undergo extensive devolatilization during prograde metamorphism. We do not discount the possibility of significant fluxes of volatiles toward the Earth's surface during prograde metamorphism in compressional regimes. Recent studies suggest that metamorphic devolatilization of the deep crust is episodic (Person and Baumgartner, 1995; Yardley, 1997). Connolly (1997b) argues that degassing of the deep crust during prograde metamorphism would generate zones of high porosity containing internally generated fluids. His computations show that there will be upward movement of multiple 'porous waves'. For the initial porosity wave generated by dehydration at depths of 12–18 km, Connolly's (1997b) modeling suggests that this wave will reach the surface ~5 Ma later. In subduction zone settings at depths of 12–15 km, it is possible that considerable carbonate could precipitate in veins or pervasively carbonate rocks overlying the subduction zone (Bebout, 1995). The relatively long pathway between mid-crustal depths and the surface may be conducive to precipitation of carbonates and, thus, diminution of the CO_2 contents of metamorphic fluids migrating toward the Earth's surface.

5.3. Eocene Himalayan and Cordilleran CO_2 degassing computed from metamorphic fluid fluxes

Using the convective hydrothermal CO_2 fluxes derived by Nesbitt et al. (1995), we reassess Eocene metamorphic CO_2 degassing in the Pakistan Himalaya and Karakoram by considering the ~ 10^5 km^2 area of Eocene metamorphism. A CO_2 flux of 3.8×10^{12} mol km^{-2} Ma^{-1} (Nesbitt et al., 1995) yields an area-integrated CO_2 flux of ~ 4×10^{17} mol Ma^{-1} for the Pakistan Himalaya and Karakoram. CO_2 fluxes derived for the Paleozoic metamorphism in New England (~ 1.5×10^{12} mol km^{-2} Ma^{-1}) yield ~ 1.5×10^{17} mol Ma^{-1}. Thus, as in our reanalysis of metamorphic CO_2 flux using mass loss calculations, as outlined in Section 2.1, we conclude that metamorphic CO_2 generated by post-collisional metamorphism in the Pakistan Himalaya and Karakoram is an unlikely cause of Early Eocene warmth.

Coupling a CO_2 flux of 1.5×10^{12} mol km^{-2} Ma^{-1}, as computed for the eastern Vermont regional metamorphism, with the ~ 2×10^6 km^2 area of Eocene extension and igneous activity in the Cordilleran belt, yields an area-integrated CO_2 flux of ~ 3×10^{18} mol Ma^{-1}. This area-integrated flux is within the range estimated by Nesbitt et al. (1995) and thus supports their contention that metamorphic CO_2 degassing in the Cordilleran belt could have significantly contributed to Eocene warming.

5.4. Miocene degassing in the Himalayan orogen

Kerrick and Caldeira (1993) suggested that CO_2 produced by the mid-Cenozoic regional metamorphism in the Himalayan belt of India, Nepal and Bhutan could have contributed to Miocene warmth. The period of mid-Miocene warming (~ 20–15 Ma; Douglas and Woodruff, 1981) correlates with rapid uplift and erosion of the Himalaya. Anatectic leucogranites dated at ~ 20 Ma represent the final products of widespread metamorphism and synmetamorphic plutonism (Noble and Searle, 1995; Searle et al., 1997). The leucogranites apparently formed by decompression melting accompanying extension and exhumation (Harris and Massey, 1994; Inger, 1994). Intrusion of the leucogranites to shallower levels would have provided heat for hydrothermal activity. Geochronology data suggests rapid cooling during the Early and Middle Miocene (Hodges et al., 1994; Searle et al., 1997). Accordingly, the 2000-km-long Himalayan belt from northwest India to Bhutan may have experienced widespread post-metamorphic extension and rapid uplift. If so, penetration of meteoric water into this regime could have caused a widespread hydrothermal event that may have promoted infiltration-driven decarbonation. An $^{40}Ar/^{39}Ar$ age of ~ 14 Ma for hydrothermal mica in an extensional fracture in north-central Nepal (Coleman and Hodges, 1995) argues for Mid-Miocene hydrothermal activity accompanying extensional tectonism. During this event, significant quantities of CO_2 could have been produced from decarbonation of abundant metapelites present in this portion of the Himalayan orogenic belt (Kerrick and Caldeira, 1993). Structural studies (Gapais et al., 1992) suggest that the Miocene extension and exhumation of the Higher Himalayan Crystalline Series occurred during convergence. Gapais et al. (1992) conclude that the rising hot basement underwent extensional spreading while the underlying crust was experiencing compression and tectonic thickening. However, structural studies of the North Himalayan shear zone also provide evidence for dextral transpressional tectonism in the Miocene (Vannay and Steck, 1995). If so, the Miocene tectonism in the Himalayan belt would have been similar to the Eocene transpressional tectonism in the Cordilleran orogen.

5.5. Metamorphic CO_2 degassing and Mesozoic paleoclimate

Other than the Eocene, there are several metamorphic belts with widespread extensional tectonism and synmetamorphic plutonism. Widespread magmatism and regional metamorphism associated with collision and subduction occurred in the circum-Pacific orogen during the Mesozoic. The temporal and genetic relationship between magmatism and low-pressure regional metamorphism has been well documented in the western United States (Barton and Hanson, 1989). Accordingly, as suggested by Kerrick and Caldeira (1993, 1994a), the global warmth during the Mesozoic could, in part, be attributed to metamorphic degassing from Mesozoic collisional belts.

5.6. Carbonate vein formation as a CO_2 sink

As noted by Kerrick and Caldeira (1993), a potentially significant sink for CO_2 in shallow crustal levels is precipitation of carbonate in veins or pervasive carbonation. Accordingly, the flux of CO_2 to the atmosphere would be diminished in proportion to the amount of CO_2 consumed in this process. Low-grade regionally metamorphosed rocks of the southern Omineca belt contain (on average) 1–2% of quartz–carbonate veins (Nesbitt and Muehlenbachs, 1995b). If we assume that the veins consist of an equal volumetric proportion of quartz and calcite (B.E. Nesbitt, pers. commun.), and that there is 1–2 vol.% of veins in the metamorphic rocks, quartz–carbonate veins would contain $1.3–2.7 \times 10^{11}$ mol of CO_2 for each km^3 of rock. If we consider a 10-km-thick section containing low-grade metamorphic rocks, and the total area of exposed low-grade metamorphic rocks in the southern Ominica belt ($\sim 1.3 \times 10^5$ km^2: Nesbitt et al., 1995, fig. 2), $\sim 1.8–3.5 \times 10^{17}$ mol of CO_2 would be tied up in quartz–carbonate veins. Assuming that the hydrothermal event lasted 10 Ma, and that the quartz–carbonate veins formed continuously during that period, then the rate of CO_2 consumption by carbonate precipitation in veins would be $\sim 1.8–3.5 \times 10^{16}$ mol Ma^{-1}. Comparing this with the $\sim 2 \times 10^{17}$ mol Ma^{-1} area-integrated CO_2 flux computed with the CO_2 flux of 1.5×10^{12} mol km^{-2} Ma^{-1} calculated from the New England metamorphic belt indicates that 9–18% of the CO_2 generated by metamorphism was lost to carbonate veins. Accordingly, we suggest that the consumption of CO_2 by precipitation of carbonate veins may not significantly decrease the amount of CO_2 in fluids that convect to near-surface crustal levels. Additional studies on the proportion of carbonate in veins and vein selvages of low-grade metamorphic rocks, and radiometric age dating of vein formation, would be very useful for further addressing this problem.

5.7. *Suggestions for future research on CO_2 degassing from the Cordilleran orogen*

The labor-intensive petrographic studies of fluid flow in New England show that paleofluxes can be determined from petrologic studies of areas a few thousand km^2. However, a similar analysis over large metamorphic belts, such as the $\sim 10^5$ km^2 area of the Eocene plutonic–metamorphic complex of the southern Ominica belt, presents a formidable task. Accordingly, it is impractical to suggest determining regional CO_2 fluxes during the Eocene hydrothermal activity in the Cordilleran belt by regional-scale petrographic studies on fluid fluxes.

From studies of regions undergoing contemporary CO_2 degassing, the flux of metamorphic CO_2 to the surface is largest in regions undergoing extensional tectonism and synmetamorphic intrusion. Decarbonation in the upper 10 km of crust is an attractive mechanism for fluxing large volumes of CO_2 toward the Earth's surface. The Cordilleran belt may be the largest of this type of tectonic regime in the Eocene. Thus, of all the Eocene metamorphic belts worldwide, the Cordilleran belt may have supplied the most metamorphic CO_2 to the Eocene atmosphere. Quantifying pluton-driven fluid flow using hydrodynamic modeling (Hanson, 1995), coupled with the exposed size, geometry and extent of the plutons and metamorphic zones exposed in the Canadian Cordillera, is our preferred approach to further assessing the CO_2 flux during the Eocene hydrothermal event in the Canadian Cordilleran belt.

Nesbitt et al. (1995) modeled the entire Eocene magmatic–metamorphic belt in the Cordillera with homogeneous crustal permeability. However, there is evidence of considerable heterogeneity throughout this belt. In the southern Ominica belt of the Canadian Cordillera (south of 52°N) there was widespread Eocene plutonism and extensional tectonism. In contrast, no Eocene intrusions are exposed in the northern Ominica belt (north of $\sim$ 52°N) and, compared to the southern Ominica belt, there is considerably less evidence for Eocene extensional tectonism (Nesbitt and Muehlenbachs, 1995b). The southern Ominica belt represents a deeper crustal level than the northern Ominica (B.E. Nesbitt, pers. commun.). The abundance of intrusives in the more deeply eroded section (the southern Ominica belt) supports the argument that deep-seated intrusions provided a thermal source for fluid convection. The Armstrong and Ward (1991) belt of Eocene magmatic activity, which was used by Nesbitt et al. (1995) to compute a metamorphic CO_2 flux in the Eocene, encompassed the northern Ominica belt. The lack of Eocene plutons in the northern Ominica belt, and the limited evidence for extension in this region, suggest that the computations of infiltration-driven metamorphic CO_2 degassing in the Cordilleran belt should be reassessed, and include only those regions with evidence of widespread fluid convection such as the southern Omineca belt.

Nesbitt and Muehlenbachs (1995b) note that fluid flow during the Eocene hydrothermal event in the southern Canadian Cordillera was largely through fractures. Thus, there was little pervasive fluid flow through the host rocks. Accordingly, a model of pervasive infiltration-induced decarbonation would be inapplicable for the production of CO_2. Consequently, the mechanism of CO_2 generation by fluid–rock interaction in the southern Canadian Cordillera requires further research.

5.8. Relevant priorities for future research on metamorphic fluid flow

Further quantification of metamorphic CO_2 degassing of metamorphic belts will require detailed studies of the heterogeneity and 3-D flow of metamorphic fluids. The recent study of Skelton et al. (1995) on fluid flow during metamorphism in the Scottish Highlands serves as a benchmark for such endeavors. Because quartz veins may represent fossil channels for fluid flow (e.g., Ague, 1997; Connolly, 1997a), particular attention should be paid to the distribution and occurrence of quartz veins in metamorphic rocks. Analysis of downflow versus upflow of metamorphic fluids will be essential for further assessing fluid transport to the Earth's surface.

5.9. Selverstone and Gutzler's (1993) analysis

Selverstone and Gutzler (1993) argued that during the Cenozoic, removal of CO_2 from the atmosphere by subduction of carbonate rocks may have been a significant factor in the post-125 Ma cooling. Their primary evidence for this hypothesis is the occurrence of carbonate, and the petrologic evidence for limited fluid flow, in eclogite-facies rocks in the Austrian Alps. We do not discount the evidence for deeply subducted carbonate or the possible role of deep subduction in carbonation of the mantle. Indeed, mantle CO_2 is manifest by several lines of evidence including kimberlites, carbonatites and fluid inclusions in MOR basalts. However, the existence of carbonate in deeply subducted rocks does not per se support their explanation of Cenozoic cooling. Sedimentary carbonate rocks (such as shelf deposits) or carbonates in metamorphic rocks represent reservoirs for CO_2 in the global carbon cycle but do not impact atmospheric CO_2 contents and, thus, global paleoclimate (Kerrick and Caldeira, 1994b). Selverstone and Gutzler (1993, p. 885) concluded that "*...continental collision events generally have only minor associated plutonism and volcanism to return carbon to the atmosphere.*" This statement conflicts with the widespread Cenozoic intrusive and extrusive magmatism in the Tethyan orogenic belt (Sengör et al., 1993). Geochronology studies show that the 2600-km-long Transhimalayan batholith had two major intrusive stages: Cretaceous (~ 100 Ma) and Paleocene–Eocene (60–45 Ma) (Debon et al., 1986). Miocene intrusive and extrusive rocks record the continuation of magmatic activity after the Eocene (Schärer et al., 1990; Searle et al., 1992; Turner et al., 1993; Inger, 1994). In addition to the Tethyan belt, there was extensive magmatism associated with collision in the Cordilleran belt (Ward, 1995). The issue here is not whether there is extensive magmatism associated with continental collision, as has been extensively documented, but the global variation of CO_2 released by igneous activity through time. Most of the volume of magmatic rocks is mid-ocean ridges (MOR) and large igneous provinces (LIPS) (Crisp, 1984). The total volume of MOR + LIPS magmatism has considerably declined since the Late Cretaceous (Kaiho and Saito, 1994); thus, the amount of CO_2 produced by magmatic degassing may have markedly decreased since the Late Cretaceous. Accordingly, we suggest that the post-125 Ma cooling reflects diminution in global magmatic activity rather than the amount of carbonate undergoing subduction (cf. Selverstone and Gutzler, 1993).

5.10. Decarbonation of subducted oceanic crust

Our analysis has been confined to CO_2 degassing related to metamorphism of crustal rocks subjected to collisional tectonism. We have not considered degassing of subducted oceanic crust. Staudigel et al. (1989) concluded that hydrothermal alteration of oceanic crust at mid-ocean ridges provides a globally significant CO_2 sink. However, oceanic crust undergoes metamorphism during subduction as a consequence of ocean–continent collision. Studies of the metamorphism of basic rocks (Bucher and Frey, 1994) illustrate that decarbonation is widespread in hydrothermally altered metabasites (greenstones) subjected to prograde metamorphism. In addition to alteration of basaltic oceanic crust, low-temperature hydrothermal alteration of serpentinites at MOR spreading centers also results in formation of carbonates (Bonatti et al., 1974). During subduction zone metamorphism, ophicarbonate rocks undergo decarbonation (Driesner, 1993) and thus release some of the CO_2 that was incorporated during sea-floor alteration. Critical to the global carbon cycle is whether the CO_2 is released at shallow levels and is thus fluxed into the overlying mantle or crust without the involvement of magmas or whether degassing occurs at greater depths and thus provides CO_2 for arc magmatism.

6. Summary

In summary, we find that:

(1) Extensional regimes with high heat flow are the environments most likely to transfer significant amounts of metamorphic carbon dioxide to the atmosphere.

(2) CO_2 degassing from the Himalaya–Karakoram belt was probably too little and too late to explain Early Eocene global warmth.

(3) CO_2 degassing from the Cordilleran belt may have caused significant Eocene global warming.

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