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Role of fluid flow in the contact metamorphism of siliceous dolomitic limestones—Reply to Hanson

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It has been recognized for more than a decade that the mineralogy of many metamorphic rocks is controlled not just by the elevated pressures and temperatures but also by pervasive flow of chemically reactive fluids during metamorphism. Until recently, however, little was known about the systematics of the control of mineral assemblage by reactive fluid flow. The motivation of the paper under discussion was to understand how mineral assemblages in two compositions of siliceous dolomitic limestone systematically change as a function of the amount and direction of fluid flow during contact metamorphism. A rigorous treatment of the problem would involve explicit consideration of phase equilibria, heat transfer, hydrology, reaction kinetics, and permeability development and the interdependence of these factors. It would be a daunting task both conceptually and computationally. To facilitate matters, a simple model was adopted that captures only the most fundamental aspects of the thermal structure of a contact aureole: elevated temperature and a temperature gradient. It was fully realized, therefore, that results of the calculations should be regarded as a bridge between little or no systematic understanding of mineral reactions driven by fluid flow and a more complete understanding that will eventually emerge from fully integrated mineralogical, thermal, and hydrologic simulations of contact metamorphism. Nevertheless, several significant generalizations emerged:

(1) Assuming final mineral-fluid equilibrium at peak temperatures, the mineral assemblage of rocks is completely independent of the thermal evolution of the aureole in the absence of reactive fluid flow. There is no aureole in which documented assemblages are consistent with both low porosity (<2%) and no infiltration by externally derived fluid. If infiltration is not involved in the contact metamorphism of siliceous dolomite, commonly observed mineral assemblages imply implausibly large porosities (>10%). Fluid-rock reactions more likely involved flowing fluid.

(2) Fluid flow in carbonate rocks during metamorphism drives surprisingly complex and unanticipated geochemical behavior. Isobaric univariant assemblages may be either spatially widespread or limited to reaction fronts both when fluid flow is in the direction of increasing temperature and in the direction of decreasing temperature. Two kinds of reaction fronts develop during up-temperature flow (e.g., f1 and f3, Fig. 5 of Ferry, 1994a) that result from qualitatively different phenomena. At a given spatial point, reactions can first go to completion gradually over a range of time-integrated flux (time) and later at a sharp front at a single value of time-integrated flux (instantaneously) or vice versa. Generally, however, isobaric univariant assemblages are spatially much more widespread when up-temperature flow occurs. Down-temperature flow tends to restrict univariant assemblages to sharp reaction fronts between reactant and product minerals.

(3) There is a hierarchy of mineral assemblages in contact metamorphosed siliceous dolomite with respect to the amount of fluid flow. For example, regardless of the direction of flow, dolomite + quartz + diopside develops only when time-integrated flux is very low. Assemblages such as tremolite + dolomite + calcite and talc + dolomite + calcite, on the other hand, form only after a threshold value of time-integrated flux is attained. Figures 5–8 of Ferry (1994a) show how mineral assemblages systematically evolve from low-flux assemblages to high-flux assemblages as a function of space, time, and flow direction.

(4) The mineralogical effects of fluid flow at any one position in an aureole typically cannot be understood without fully accounting for all mineral reactions upstream. The development of periclase during up-temperature flow, for example, can occur only after flow and reaction upstream have exhausted the capacity of rocks to buffer fluid composition to X_{CO_2} greater than that defined by dolomite + periclase + calcite at the contact. Formation of periclase, therefore, can be understood only after all reactions upstream are identified and their buffer capacity is evaluated.

(5) Some equilibria such as dolomite + quartz + talc + calcite correspond to isobaric T-X_{CO_2} curves that monotonically increase in X_{CO_2} with T but that have inflection points. In the absence of flow, reaction progress, ξ, in these assemblages is proportional to X_{CO_2} and hence T. Reaction progress, therefore, increases monotonically with increasing grade. When fluid flows in the direction of increasing temperature, however, ξ is inversely proportional to the slope of the T-X_{CO_2} curve. Reaction progress in this case increases with increasing grade to a maximum (at the inflection point) and then decreases. This potentially allows discrimination between no flow and up-temperature flow during metamorphism.

(6) When magmatic H_2O flows horizontally down-temperature into carbonate rock, an O isotope alteration front develops, the position of which can be tracked relative to mineral isograds. In the case of the model siliceous dolomite, the isotope front should be very near the periclase isograd but slightly closer to the pluton (Fig. 7 of

Ferry, 1994a). At lower grades in the aureole, mineral assemblages provide useful information about metamorphic fluid flow, whereas stable isotope compositions do not.

(7) The identity and distribution of mineral assemblages predicted by the calculations bear a striking resemblance to those observed in contact aureoles containing siliceous dolomite. Assemblages corresponding to flow both in the direction of increasing and decreasing temperature occur. Except where periclase is developed more than ~100 m from the contact, the amount of fluid involved in contact metamorphism of siliceous dolomite, expressed as a time-integrated flux, is typically small, on the order of 100–200 mol/cm^2. For values this small the effect of fluid flow on heat transfer is not large (Hanson, 1995, his Fig. 1).

Hanson's comments disprove none of these generalizations. His critique fails because it exclusively considers the physics of contact metamorphism without any explicit consideration of chemistry or petrology. His calculations make not one specific prediction about mineral stability in contact metamorphosed carbonate rocks.

The controversy implied by this discussion and reply is really a difference in perspective rather than substance. Hanson approaches contact metamorphism from the standpoint of forward modeling. An intrusion with specific size, geometry, and temperature has a well-defined energy that can heat an aureole, drive fluid flow, and promote mineral reactions. Given an aureole with specified initial temperature, permeability structure, and other physical properties, the temperature in the aureole can then in principle be computed as a function of space and time. Temperature in forward models is a dependent variable constrained by the initial energy of the system that is conserved in the calculations. My approach is that of a field petrologist and is from the standpoint of inverse modeling. Mineral equilibria in a specific aureole define a temperature gradient. For example, Equation 1 of Ferry (1994a) describes the temperature profile in the Boulder aureole, Montana, within error of measurement by calcite + dolomite thermometry (Rice and Shaffer, 1994; and personal communication). The question posed by such an aureole is, what amount and geometry of fluid flow is consistent with observed mineral assemblages and the inferred temperature profile? Therefore, models are developed like those in Ferry (1994a) that compare mineral assemblages on an equal-temperature rather than equal-energy basis. The energy of the system is considered to be a dependent variable, the value of which adjusts accordingly to be consistent with observed assemblages, inferred temperature, and time-integrated flux. Energy conservation is completely irrelevant to the problem (which is one of mass balance alone). Calculated results, therefore, cannot somehow "violate" conservation of energy, which is not a premise of the models implicitly or otherwise.

Without a doubt the boundaries of assemblage fields and the reaction progress contours in Figures 3–8 of Ferry (1994a) will be different when more sophisticated calculations consider time-dependent temperature, reaction kinetics, permeability development, and other issues. Hanson's comments, however, provide no understanding of how large these differences might be. His Figure 1 nevertheless is cause for cautious optimism. The approach of Ferry (1994a) errs to the extent that temperature and temperature gradients change during fluid flow. In Hanson's calculations that integrate fluid flow, time-dependent temperature, and enthalpy of reaction, temperature deviates from the maximum value by no more than ~20° during flow 0.25 and 0.75 km from the contact for a time-integrated input fluid flux of 200 mol/cm^2. Temperature gradients appear almost independent of the amount of flow and enthalpies of reaction. A steady-state temperature profile during flow and mineral-fluid reaction may not have been a hopelessly bad approximation either in the study of Ferry (1994a) or in petrologic investigations of metamorphic fluid flow generally.

The most important of Hanson's contentions to refute is his claim that ". . . it is impossible and potentially misleading to characterize important aspects of metamorphic fluid flow independent of an understanding, or at least an accounting, of the physical mechanisms of heat and fluid transfer." Although it is beyond the scope of this reply to discuss every assemblage considered by Ferry (1994a), a selected number of examples and one case study demonstrate that this and similar statements in Hanson's comment are incorrect.

(1) The assemblage dolomite + quartz + tremolite + calcite develops at 1 kbar only between 422 and 466 °C and only in the presence of fluid with $X_{CO_2} = 0.710–0.975$ (Ferry, 1994a, Fig. 1). In this interval $(\partial X_{CO_2}/\partial T)_P$ for the equilibrium is in the range $(2.43–9.65) \times 10^{-3}$. Considering Equation 9 of Ferry (1994a), time-integrated flux for horizontal up-temperature flow, q, is related to reaction progress in the assemblage by $q = (283.7 - 473.3)\cdot[\xi/(dT/dz)]$ mol/cm^2. In portions of the aureole where $T = 422–466$ °C the horizontal thermal gradient, dT/dz, does not vary greatly; plausible values are in the range 80–320 °C/km (e.g., Hanson, 1995, his Fig. 1C; Furlong et al., 1991). Time-integrated flux, therefore, may be related to reaction progress by $q = (2.29 \times 10^5)\xi$ mol/cm^2 with an uncertainty of a factor of 2.6 without any consideration of peak temperature or the mechanisms of heat and fluid transfer in the aureole. The uncertainty can be reduced if there is independent information about the temperature of reaction (e.g., from calcite + dolomite thermometry).

(2) Periclase develops at 1 kbar only at temperatures between the peak value at the contact (650 °C in the models) and the temperature of the periclase + brucite + calcite + dolomite isobaric invariant point and only in the presence of fluid with $X_{CO_2} = 0.037–0.098$ (Ferry, 1994a, Fig. 1). When periclase in the model siliceous dolomite forms at a reaction front driven by outward flow of H_2O fluid from the contact, the distance, z, of the periclase isograd from the contact is, therefore, simply

related to molar time-integrated input flux (obtained from Eq. 15 of Ferry, 1991). The relation is $q = (15.5)(\xi_{mx})(z)$ with an uncertainty of a factor of 1.7, where ξ_{mx} is progress of the periclase-forming reaction when it has gone to completion. The result requires an estimate of peak temperature at the contact but no other information about heat transfer in the aureole. The uncertainty can be reduced by any reasonable assumption about temperature along the flow path (e.g., temperature decreases).

(3) Because of the small temperature dependence of the mineral-fluid O isotope fractionation factor, α, the position of any O isotope alteration front resulting from down-temperature flow of magmatic fluid into siliceous dolomite is independent of temperature in the aureole (Dipple and Ferry, 1992). Therefore, curves like the dashed ones in Figures 7 and 8 of Ferry (1994a) are independent of any consideration of temperature or heat transfer in the aureole.

The Alta aureole, Utah, illustrates how field observations and considerations of petrologic and isotope data interpreted only with principles of mass balance can lead to a first-order understanding of the geometry and amount of fluid flow in a contact aureole. Pressure during contact metamorphism was ~750 bars, and peak temperature at the contact was ~626 °C (Cook and Bowman, 1994). Periclase and calc-silicate skarns are developed on a bed-by-bed basis (Bowman et al., 1994). Because bedding is nearly horizontal, metamorphic fluid flow must have been as well. Assemblages in the low-grade portions of the aureole record fluid compositions with $X_{CO_2} > 0.2$ (Moore and Kerrick, 1976). At 750 bars periclase develops only when $T > 587$ °C and $X_{CO_2} > 0.043$; the upper limit on X_{CO_2} is 0.096 for a peak contact temperature of 626 °C. Because none of the prograde reactions observed in the aureole is capable of buffering fluid composition from $X_{CO_2} > 0.2$ to $X_{CO_2} < 0.1$, periclase must have developed from horizontal down-temperature rather than horizontal up-temperature fluid flow. This conclusion is independent of details of the thermal evolution of the aureole and agrees with that of Bowman et al. (1994). Assuming that rocks in the Alta aureole have compositions that can be represented by the model siliceous dolomite in Ferry (1994a), and considering that the periclase isograd is located ~200 m from the contact (Bowman et al., 1994; Cook and Bowman, 1994), the time-integrated flux associated with formation of periclase in the aureole, computed following the methods described above, is 975–2310 mol/cm^2. An O isotope alteration front is observed in the aureole (Bowman et al., 1994). Although the precise location of the front is impossible to measure because it has been smeared out by dispersion, it is located approximately 100–200 m from the contact. The time-integrated flux associated with formation of the isotopic front, computed following the methods described above, is 845–1690 mol/cm^2. Assuming a molar volume of the fluid of 60 cm^3/mol, the time-integrated flux estimated from these simple considerations of the location of the periclase isograd and isotope alteration front agrees well with the estimate of Bowman et al. (1994), 370–1350 mol/cm^2, on the basis of a more elaborate analysis of the isotope data.

These examples and the case study illustrate that Hanson's contention that energy balance is a higher authority over mass balance and that important information about fluid flow in contact aureoles can never be obtained without accounting for heat transfer is untrue. Petrologists are fortunate that fundamental aspects of metamorphic fluid flow can often be inferred from phase equilibria, mass balance relations, and field observations without prior recourse to a full-blown thermal model of the terrane.

It has been known from the beginning of metamorphic petrology that contact aureoles heat and cool. It has been known for decades that the thermal budget of contact aureoles and geothermal fields is controlled to one degree or another by fluid flow and chemical reactions (reviews by Furlong et al., 1991, and Ferry, 1994b). Therefore, it is hoped that no one mistook the model calculations of Ferry (1994a) as a rigorous simulation of contact metamorphism. Now that the systematics of mineralogical evolution in siliceous dolomite metamorphosed with fluid flow along a steady-state temperature profile are understood, new studies need to explicitly integrate fluid flow, heat transfer, and mineral reaction. We need more calculations like Hanson's but ones that incorporate the chemistry of fluid-rock interaction. Only then can the shortcomings or strengths of the calculations by Ferry (1994a) be meaningfully evaluated. If this discussion and reply motivate such a study, then they will have served a purpose.

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