DISCUSSION

COMPOSITIONAL VARIATIONS IN METAMORPHOSED SEDIMENTS OF THE LITTLETON FORMATION, NEW HAMPSHIRE

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INTRODUCTION

Moss and others (1995) and Moss, Haskin, and Dymek (1996) obtained new chemical analyses of rocks from the Littleton Formation; their research represents a significant contribution to the data of geochemistry for metamorphosed clastic sediments. Furthermore, their results strongly suggest that the geochemical systematics of the Littleton Formation are more complex than Ague (1991) realized. Moss and coworkers used their chemical data to draw conclusions about the amount and nature of element redistribution that occurred during the metamorphism. For example, Moss, Haskin, and Dymek (1996) concluded that there was “... macroscopic separation and mobilization of SiO₂ (and perhaps other elements) during metamorphism...”. On the other hand, they did not find evidence of systematic, long-range, net gain of loss of SiO₂. However, it appears that, for many elements, systematic local or long-range element mobility could have easily gone undetected in the studies of Moss and coworkers. I would urge caution, therefore, before using the results of Moss and others (1995) and Moss, Haskin, and Dymek (1996) as general models for mass transfer during regional metamorphism of clastic sediments.

RELATIONS BETWEEN LOCAL AND REGIONAL MASS TRANSFER

In order to obtain a broader perspective on the question of element mobility, it is useful to compare the chemical data of Moss and coworkers for the Littleton Formation with the data of Ague (1994a, b) for the Wepawaug Schist of Connecticut. Mass balance analysis (Ague, 1994a, b) indicated that silica was lost from some of the garnet zone rocks and many of the staurolite and kyanite zone rocks during metamorphism of the Wepawaug Schist. Ague (1994b) concluded that this silica depletion resulted from diffusional transport of silica from wallrocks to cracks. These cracks are now preserved as quartz veins. The silica transport resulted in the formation of silica-depleted wallrock alteration selvages adjacent to the veins; the total thickness of the selvages varies from ~1 to ~10 cm (Ague, 1994b, fig. 8). Silica depletion adjacent to veins has also been observed in other metamorphic settings (compare Yardley, 1975; Fisher and Brantley, 1992; Erslev and Ward, 1994). This silica mass transfer was “local” in the sense that it occurred on the scale of hand samples. How was the “local” mass transfer related to the regional migration of metamorphic fluids? This question is basic to the whole problem of element mobility during metamorphism and is worth examining in detail here.


A. Fracturing, Fluid Flow, Regional Mass Transfer

- Regional down-T fluid flow; some quartz precipitation in cracks
- Chemical and isotopic exchange between fluid and crack walls; mobile elements include alkali and alkaline earth metals, Mn, Cu, Zn, P

B. Crack Healing

- Cracks heal as a result of silica transport from wallrocks to cracks; wallrocks become depleted in silica

C. Net Result of Repeated Fracturing, Fluid Flow, and Crack Healing

- Chemical and isotopically altered selvage (strongly depleted in silica)

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Fig. 1. Model of vein formation and wallrock alteration processes inferred to have affected amphibolite facies (staurolite and kyanite zone) pelitic rocks of the Wepawaug Schist. (A) Fracturing, fluid flow, and regional mass transfer. Fluid advection through cracks denoted by heavy arrows. Some advection may also occur in the immediately adjacent wallrock. Chemical and isotopic exchange between migrating fluid and crack walls denoted by small arrows. (B) Crack healing. Silica transport from wallrocks to cracks (denoted schematically by arrows). Some fluid flow may also occur during this stage. (C) Net result of many repeated fracturing, flow, and healing episodes. Quartz veins shown with stipple pattern; selvages shown with horizontal rule. Most veins in the Wepawaug Schist are between ~1 cm and ~10 cm thick; typical vein thickness is 2 to 3 cm. Hypothetical rock samples I and II discussed in text.
Ague (1994a, 1995) advanced a model in which local-scale formation of selvages in amphibolite facies pelitic rocks of the Wepawaug Schist was the direct result of regional flow processes; the major features of the model are shown in figure 1. First, cracks formed in the rock as a result of processes such as hydrofracturing (fig. 1A). Regional fluid migration was focused preferentially into these cracks because they were zones of elevated permeability. In the case of the Wepawaug Schist, both petrologic and stable isotopic evidences suggest that the cracks were loci for the regional, down-temperature migration of metamorphic fluids (Ague, 1994b; 1995; van Haren, Ague, and Rye, 1996). Some silica was deposited in the cracks during fluid flow in response to decreases in temperature and pressure along the regional flow path. In addition, mass exchange between the fluids and the crack walls (involving primarily alkali and alkaline earth metals, Cu, Zn, Mn, and P) occurred during the flow. The second stage of the process was crack healing (fig. 1B). At some time after cracking occurred, silica diffused toward the cracks (zones of low pressure relative to the wallrock) in order to heal the cracks (see Yardley, 1975; Fisher and Brantley, 1992). The occurrence of crack-seal textures (Ramsay, 1980) in veins throughout the Wepawaug Schist (Ague, 1994b) strongly suggests that the vein-wallrock contacts were zones of mechanical weakness that underwent repeated fracturing during vein formation. The net result of many coupled cracking, flow, and healing episodes was the production of chemically and isotopically altered, silica-depleted selvages adjacent to macroscopic flow conduits (fig. 1C). Amphibolite facies pelitic rocks adjacent to veins lost significant silica (and volume) at the hand sample scale during metamorphism (fig. 1B), but local and regional mass balance analyses indicate that entire outcrops gained silica (about 10 percent relative to low grade outcrops) as a result of silica precipitation in veins during metamorphic fluid flow (fig. 1A; compare Ague, 1994b, 1995). Vein-related chemical alteration appears to have been less intense in the upper greenschist facies (garnet zone).

The relations shown in figure 1 suggest that vein formation can result in highly differentiated outcrops that pose special challenges for sampling and geologic interpretation. For example, consider hypothetical sample I shown on figure 1C. This sample lies between selvages, and, consequently, it may have undergone only minor isotopic and chemical alteration. A mass transfer study done entirely on samples collected in between selvages (like sample I) will probably conclude that little element mobility occurred during the metamorphism. On the other hand, a study focused entirely on selavage samples (like sample II in fig. 1C) will overestimate significantly the amount of mass transfer. The studies of Ague (1994a, b) included both types of samples, and, consequently, a large range of compositions was found for the highly veined outcrops (see, for example, Ague, 1994a, fig. 20; Ague, 1994b, fig. 16).

These relations make it critical that the geologic context of the Littleton Formation rocks studied by Moss and others (1995) and Moss, Haskin, and Dymek (1996) be known in detail. From the discussion in Moss and others (1995), however, it appears that much of the original sample material is no
longer available, and, consequently, it is impossible to test the full spectrum of mass transfer hypotheses with their data set. Thus, for example, the hypothesis that veins played a significant role in the geochemical and isotopic evolution of the Littleton Formation remains to be tested. Furthermore, was the "local" mass transfer documented by Moss, Haskin, and Dymek (1996) related to regional flow processes? It is interesting to note in this regard that Chapman (1950) described what appear to be staurolite-rich, silica-depleted alteration selvages around quartz veins in the Littleton Formation. The importance of these veins in terms of local and regional mass transfer must, however, be addressed by future investigations.

WHAT CAN BE SAID ABOUT THE LITTLETON FORMATION?

Moss, Haskin, and Dymek (1996, p. 488-494) carefully investigated silica mobility using both their results and those of Moss and others (1995). Moss, Haskin, and Dymek (1996) suggested that the Zr-SiO₂ systematics of most of their samples, regardless of metamorphic grade, were the result of sedimentary processes. They concluded, therefore, that there was no evidence for systematic, long-range, net gain or loss of SiO₂. Moss and coworkers did not, however, present a similar discussion for any of the other elements. Silica cannot be considered in a vacuum. The logic employed to interpret silica mobility must be used for all elements under the constraints imposed by the composition of the inferred protolith (the low grade rocks) and the geochemical reference frame (Zr). The results can then be examined to see if they actually make sense.

A fundamental conclusion reached in Shaw’s (1956) classical study of the Littleton Formation was that rocks lose volatiles with increasing metamorphic grade. Therefore, a simple, objective test of any mass balance analysis is that the analysis should be able to detect volatile loss with increasing metamorphic grade. Consider, for example, the loss on ignition (LOI), which approximates rock volatile content (mainly H₂O + CO₂). Using the methods of Moss and coworkers, I have made a plot of Zr versus LOI for the full Littleton data set comprising the results of both Moss and others (1995) and Moss, Haskin, and Dymek (1996) (fig. 2A). Clearly, there is significant overlap between the compositional fields for all rocks, regardless of grade. Thus, one might come to the awkward (and erroneous) conclusion that there is no evidence for systematic, long-range, net gain or loss of volatiles.

The mass balance relations for the other major and minor elements were summarized by plotting mass change values calculated using (Ague, 1994a):

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\frac{\text{Final Mass } j - \text{ Initial Mass } j}{\text{Initial Mass } j} = \left[ \frac{C_0^i}{C_i'} \left( \frac{C'_j}{C_j} \right) - 1 \right],
\]

(1)

where C is concentration, j denotes a "mobile" species, i denotes an "immobile" reference species (Zr), and the superscripts 0 and ' denote the protolith and the "altered" rock, respectively. If protolith compositions and the geochemical reference frame are well constrained, then eq (1) yields true
Fig. 2(A) Zr (ppm) versus LOI (loss on ignition, in wt percent) for the Littleton Formation. Sample set identical to the one used by Moss, Haskin, and Dyck (1996) in their figure 5. Note lack of strong evidence for loss of volatiles with increasing metamorphic grade. High grade sample with lowest Zr and LOI concentrations is L36b, a sample which Moss and others (1995) consider to be “modally unrepresentative” of the outcrop from which it was taken. (B) Al₂O₃ versus LOI (both in wt percent); same samples as in part (A). Strong positive correlation between Al₂O₃ and LOI for the low grade rocks reflects clay content of original sediments (clays are the primary hosts for both Al and volatiles). General trend expected for volatile loss indicated by heavy black arrows. Note strong evidence for volatile loss from the medium and high grade rocks.
percentage mass changes. For the Littleton data set, however, it is critical to point out that until geologic relations are better known, the calculated values should be regarded as apparent, not actual, mass changes (see below). The results using Zr as the reference species are presented in figure 3. The results for high grade rocks relative to low grade rocks are particularly surprising because, with the exception of LOI and SiO₂, all elements in the high grade rocks show apparent mass gains of large magnitude. As expected from figure 2A, no statistically significant mass loss is evident for LOI for the medium or high grade rocks. The apparent mass changes shown in figure 3 are highly suspect given the failure of the mass balance analysis to detect volatile loss with increasing grade. This failure is even more noteworthy considering that the high grade sample set comprises highly dehydrated rocks of the sillimanite-muscovite zone and the granulite facies.

The results in figures 2A and 3 indicate that a mass balance analysis using the data of Moss and coworkers together with a Zr reference is problematic and cannot be used to make reliable inferences about the local or long-range mobility of volatiles, silica, or other constituents. Consequently, calculations using eq (1) with Al₂O₃ as a reference were done (figs. 2B and 4). Moss and others (1995) also used an Al₂O₃ reference frame, but they did not include the data of Moss, Haskin, and Dymek (1996) in their calculations. Figures 2B and 4, on the other hand, include the data of both Moss and others (1995) and Moss, Haskin, and Dymek (1996). The computation results appear to be more reasonable—at least mass loss of volatiles from the medium and high grade rocks is indicated (apparent mass changes for LOI are −28 and −37 percent for the medium and high grade rocks, respectively; figs. 2A and 4). Other apparent mass changes, relative to low grade rocks, include (fig. 4): (1) systematic apparent enrichment of MnO and CaO in the medium and high grade rocks, (2) apparent enrichment of Na₂O in the medium grade rocks, and (3) apparent depletion of silica (about −30 percent mass change) from the high grade rocks. The rock volume change implied by the silica loss is considerable—about −20 percent. It is interesting to compare these results with those of earlier studies. For example, relative to low grade rocks, Shaw (1956) and Ague (1991) also found evidence for elevated Na₂O and CaO, and Ague (1991) found evidence for diminished SiO₂. The calculations using Al₂O₃ as a reference (fig. 4) may provide a reasonable picture of potential element mobility, but definitive resolution of the problem must await future studies that constrain carefully the geologic contexts of low, medium, and high grade samples. Ambiguities notwithstanding, the relations shown in figures 3 and 4 emphasize an important fact: regardless of the reference frame, the Littleton data set of Moss and coworkers fails to support an “isochronal” metamorphic model.

The results of Ague (1994a, b, 1995) focused on the relationships between rock composition, element transfer, and macroscopically observable metasomatic veins. The compositions of individual sedimentary layers could be traced from little altered wallrock to highly altered selvages, thus eliminating many of the fundamental ambiguities that are inherent in Moss and coworkers’ experimental design. Moreover, although the Littleton For-
Fig. 3. Apparent mass changes (see text) computed using Zr as the geochemical reference species. The data set is comprised of the low, medium, and high grade rocks of Moss and others (1995) and the average outcrop compositions for sites NH-14, NH-15, M8, M11, M12, M13, and M15 of Moss, Haskin, and Dymek (1996). Following Moss and others (1995), data for samples L6, L36a, and L36b were excluded from the calculations. Calculation methods follow Ague (1994a) and Ague and van Haren (1996). Vertical black bars are 95 percent confidence intervals computed using the calibrated bootstrap percentile method (a nonparametric method; see Efron and Tibshirani, 1993 and Ague and van Haren, 1996 for detailed discussion). “Best estimates” for apparent mass change denoted by open circles. Mass changes for oxides whose confidence limits overlap the 0 percent mass change line are inferred to be statistically insignificant.
**Oxide**

Fig. 4. Apparent mass changes computed using Al₂O₃ as the geochemical reference species. See caption of figure 3 for additional explanation. Moss and others (1995) also used Al₂O₃ as the reference species; their results differ from the results presented here because I have included the data of both Moss and others (1995) and Moss, Haskin, and Dymek (1996) in the calculations.
similar results regardless of the geochemical reference frame chosen (for example Ti, Zr; Ague, 1994a, b).

It is also worth noting that many important mass transfer phenomena in the crust take place at 1 to 10 km length scales. The rocks studied by Moss and coworkers were collected over an immense area in the States of New Hampshire and Maine. The average density of sampled outcrops is around 1 outcrop per 350 km². The coarseness of sampling would be a serious barrier to the identification of meso-scale metamorphic hydrothermal systems, such as the “hot-spots” studied by Chamberlain and Rumble (1988).

CONCLUDING REMARKS

Current studies suggest that Barrovian metamorphism can occur under conditions that are either “closed” or “open” to local or regional migration of non-volatile elements. Geochemical and isotopic data from both “open” and “closed” systems are inherently valuable. For example, “open” systems can provide information about regional fluid flow paths, fluid-driven heat transport, and the dynamic geochemical and mineralogical evolution of the middle and lower crust during orogenesis. As emphasized by Moss and others (1996), “closed” systems will largely retain the chemical systematics of sedimentary protoliths and can, therefore, be used to constrain sedimentary provenance and the tectonic settings of ancient sedimentary basins. It is an important challenge for petrologists to establish the geologic, geochemical, and isotopic criteria necessary to distinguish between “open” and “closed” metamorphic systems; the results of Moss and others (1995) and Moss, Haskin, and Dymek (1996) provide important new data for this effort.

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REFERENCES


Discussion


EDITORS’ NOTE:

The authors of the articles discussed (Moss, Haskin, and Dymek, 1995 and Moss, Haskin, Dymek, and Shaw, 1995) have elected not to reply.

Publication of this discussion does not indicate an endorsement by the Journal of Professor Ague’s point of view.