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COMPOSITIONAL VARIATIONS IN METAMORPHOSED SEDIMENTS OF THE LITTLETON FORMATION, NEW HAMPSHIRE, AND THE CARRABASSETT FORMATION, MAINE, AT SUB-HAND SPECIMEN, OUTCROP, AND REGIONAL SCALES

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ABSTRACT. Rocks from several outcrops of low-grade Littleton Formation and laterally equivalent Carrabassett Formation were analyzed for major elements and Zr. Compositional variations well outside analytical uncertainties were observed, in order of increasing magnitude, for the following: 10-g subsamples from a 2-kg hand sample of visually homogeneous slate; 100-g samples taken 10 m apart in the same outcrop; 10-g subsamples from a visually homogeneous quartzite; samples of relict turbidite beds in the same outcrop; and single 100-g samples from seven outcrops. We regard these variations as inherited from the sedimentary protolith with little if any alteration over distance scales of centimeters or greater. All could be modeled successfully as mixtures mainly of clay, quartz, and chlorite-mica, although the compositions of the clay and the chlorite-mica components had to be adjusted for different sets of samples, within reasonable bounds for sedimentary-diagenetic minerals. Compositional variations and trends in 2-kg samples of higher-grade Littleton rocks are essentially the same as for the low-grade samples. For example, SiO_2 and Zr correlate positively, as expected for sedimentary sorting of quartz and zircon from clay, but not for selective metamorphic mobilization of silica. Also found was centimeter-scale separation of K_2O from Al_2O_3 and strong covariation of Zn with Al_2O_3 in ~10-g subsamples of a staurolite schist, compositional evidence of element transport over distances of a few centimeters. Because the protolith includes at least two major, Al_2O_3-bearing components in variable proportions, element ratios to Al_2O_3 can vary such that variation in metamorphic rocks need not be a sensitive indicator of element mobility relative to Al_2O_3 even if Al is immobile.

The population of low-grade rocks encompasses a broad compositional range. Thus, it is not feasible to obtain a sample average with a small standard deviation. It would also be difficult to demonstrate conclusively whether a set of samples was representative of its metamorphic grade, or whether rocks of all metamorphic grades developed from the same combination of protolith compositions and physical characteristics.

INTRODUCTION

Compositional changes necessarily occur as sedimentary rocks are converted to metamorphic rocks. It is self evident that chemical elements must migrate during metamorphism over the short distances required to accommodate changes in mineralogy. However, other than loss of vola-

tile substances, element mobility on the scale of a hand-specimen and beyond may or may not occur in a particular formation. Recently, several investigators (Ferry, 1982; Ague, 1991) have proposed substantial gain (or loss) of elements on a large scale during metamorphism of pelites.

This paper addresses the difficulty of demonstrating whether or not large-scale element mobility has, in fact, occurred during regional prograde metamorphism. Specifically, we report the results of a detailed study of compositional variations within the Devonian Littleton Formation, New Hampshire (and the laterally equivalent Carrabassett Formation, Maine). During metamorphism of these formations, the mineralogy changed drastically, from a sedimentary-diagenetic assemblage of clays, quartz, and minor constituents, to a series of metamorphic assemblages containing garnet, staurolite, sillimanite, et cetera, depending on grade. In many outcrops, quartz veins are visible, whereas in some high-grade areas, migmatitic banding developed. Clearly, some chemical elements were mobilized. The question of concern here is how we might determine the distance scale of mobility of non-volatile elements (other than H, C, et cetera) during metamorphism, and especially whether there is geochemical evidence for regional (larger than 100-m scale) gain or loss of an element as a consequence of metamorphism.

To determine the distance scale for net movement of elements during metamorphism, we must find unequivocal differences in chemical compositions between unmetamorphosed sediments and their metamorphic equivalents (or between low-grade metasediments and equivalents of higher metamorphic grade). There are at least two methods by which such compositional differences might be demonstrated. The first is based on systematic and general gain or loss of an element with progressive metamorphism (1 and 2 below). The second depends on observation of interelement concentration trends that are produced by metamorphic reactions and the distance scale over which those trends are observed (3 below).

1. Rock samples of different metamorphic grades might be obviously and systematically different in composition.—Suppose all high-grade Littleton-Carrabassett metasediment samples had concentrations for some elements that were entirely outside the compositional range found for samples of lower grades, *and* there were sound reasons why those differences arose from metamorphic processes. In such a case, we might expect a systematic pattern of element loss or gain with intensity of metamorphism. In the case of the Littleton-Carrabassett sediments, this guideline is not applicable, because compositional ranges for samples of different metamorphic grades overlap substantially, perhaps entirely (Shaw, 1954, 1956; Moss and others, 1995). Also, rocks of higher metamorphic grade were formed in restricted geographical areas rather than throughout the region occupied by the Littleton-Carrabassett Formations. Because of this, even if systematic differences had been found, we would still have to convince ourselves that they did not reflect a lateral gradient in protolith composition.

2. Average compositions of higher-grade rocks might be significantly different from those of lower-grade rocks.—Even if element concentration *ranges* overlap, *average* element concentrations or *average* concentration ratios might differ significantly. Accurate determination of the values of the averages requires representative sampling of each metamorphic grade. Also, if differences are to be interpreted in terms of element mobility during metamorphism, then rocks of all grades must derive from the same sedimentary protolith. The protolith does not have to be homogeneous, but it must have had the same average original compositional and physical characteristics for all metamorphic grades.

In a pioneering study of compositional change caused by metamorphism, Shaw (1954, 1956) examined Littleton samples metamorphosed to low (biotite-chlorite zone), medium (garnet and staurolite zones), and high (sillimanite zones) grades. He found that the compositional ranges for all grades overlapped and did a statistical analysis based on his average composition for each metamorphic grade. His principal conclusion was that, except for volatile substances, concentrations of most elements remained constant during metamorphism. Shaw did not demonstrate that the sample sets he used were representative of their metamorphic grades or that the rocks of all grades derived from protoliths of common compositional and physical character. Because he found essentially the same average composition for the rocks of all grades, these considerations were not explored.

Moss and others (1995) reanalyzed Shaw's samples at higher precision and for more elements. They found statistically significant differences in interelement ratios between sample sets of different metamorphic grade but no pattern of increasing element loss or gain with intensity of metamorphism. They showed, however, that because intersample variability within each grade was large, average compositions were poorly constrained. Moss and others concluded that the lack of closely determined average compositions for the Littleton Formation makes the method of comparing averages insensitive to systematic changes of the order of ~10 to 20 percent for major elements and even greater for minor and trace elements. Also, in order to use averages, both representative sampling and lateral homogeneity of the sedimentary protolith are required but neither was demonstrated. These demonstrations would require knowledge of local (hand-specimen- to outcrop-scale) and regional (kilometer-scale) compositional variability of both the sedimentary protolith and the rocks of each metamorphic grade.

3. Trends of interelement concentrations over a given distance might principally reflect either compositional variations inherited from the sedimentary protolith or compositional variations produced by metamorphic reactions.—The use of interelement trends depends on observing such trends over different distance scales. Sedimentary rocks presumably have characteristic compositional variations over local and regional distance scales. For example, K and Al are associated with clays in pelites and plot on a positive trend as the proportions of clay vary from sample to sample. Over the small

distance scale of metamorphic mineral formation, at least some of these interelement correlations will be replaced by trends resulting from metamorphic reactions. Thus, a negative correlation between K and Al can appear in staurolite-rich metapelites, because Al is enriched in staurolite and K is excluded from it (shown below). Metamorphic interelement trends may appear over distances considerably greater than that of porphyroblast growth. By determining the scale over which interelement trends of the sedimentary protolith have been replaced by metamorphic trends, we could obtain information about the distance scale for net element transport. On distance scales exceeding those of metamorphic element transport, trends of the sedimentary protolith should still be preserved in metamorphic rocks. Characteristic distance scales may be different for different elements such that, at a given distance scale, sedimentary interelement patterns might be preserved for some elements but not others. The distance scale should also vary among different rock formations.

Sampling was insufficient to enable Moss and others (1995) to distinguish between metamorphic and sedimentary interelement trends in their Littleton data. Here, we report the first results of a follow-up study designed to characterize the extents of and determine the causes of, major-element compositional variability among low-grade metasediments of the Littleton and Carrabassett Formations at different distance scales—centimeters, meters, and kilometers. Compositional variability (or heterogeneity) of the type observed in the samples from the Littleton-Carrabassett Formations has traditionally been regarded as a "sampling problem." That we might expect sampling to be a problem on a small scale is evident from the visual heterogeneity of many Littleton and Carrabassett outcrops. A typical approach to sampling of such material to obtain a compositional average is to collect large samples and hope that such heterogeneities "average out" or to collect sufficient samples of different-looking materials and weight them according to their relative abundance in constructing the average. Here, instead, we exploit this heterogeneity and its associated interelement correlations as a tool to learn more about the sedimentary and metamorphic history of Littleton-Carrabassett rocks.

Compositional changes that take place between accumulation of clastic debris and the end of diagenesis are important but are not of concern here. Rather, our concern is to characterize the compositional heterogeneity over various distance scales in the protolith from which we may regard the metamorphic rocks of the Littleton and Carrabassett Formations to have developed. Because the Littleton-Carrabassett rocks began as sedimentary systems, we must assume sedimentary compositional characteristics as our baseline. In the present study, we can only detect results of metamorphic processes that rearrange elements to produce compositional characteristics that are distinguishable from sedimentary characteristics. We make the reasonable assumption that the compositions of the Littleton-Carrabassett rocks of lowest metamorphic

grade will correspond most closely to the compositional characteristics of their sedimentary protoliths.

Thus, as a starting hypothesis, we will consider that the low-grade samples inherit and retain most of the spatial pattern of compositional heterogeneity of the protolith over distances of the order of centimeters and greater. We will test this hypothesis by considering compositional trends that should differ between sedimentary and metamorphic processes. We will also test it by modelling the compositions of low-grade rocks in terms of mixtures of ordinary sedimentary endmember components. The results of this modelling show that the compositional characteristics of the low-grade rocks reasonably reflect those expected for mixtures of sedimentary-diagenetic minerals. If we assume that the compositional characteristics of the low-grade rocks are essentially those of the sedimentary protolith, then the data for the low-grade samples provide a baseline of information against which to evaluate evidence for element mobility over various distance scales during the conversion of sediments or low-grade metamorphic rocks from the same protolith to metamorphic rocks of higher grade.

EXPERIMENTAL DESIGN AND PROCEDURES

Samples corresponding to different aspects of the experimental design are summarized in table 1. Sample numbers apparently missing from the table are those of samples taken and numbered in logical sequence in the field but not yet analyzed.

Centimeter scale compositional variations.—For our centimeter-scale experiments, we concentrated on samples from two outcrops of low-grade rocks. These are Slate Ledge, New Hampshire (Billings, 1937) in the Littleton chlorite zone (slates, the NH14 sample suite), and Kingsbury, Maine (Ludman, 1978) in the Carrabassett biotite zone (quartzites, M12 sample suite) (see fig. 1 for maps). In the field, the Slate Ledge outcrop is visually uniform except for regions that contain pyrite, whereas the Kingsbury outcrop shows prominent graded bedding. Several samples representing the dominant lithologies were collected and analyzed from each outcrop. Polaroid photographs were taken in the field and marked to document the exact locations where samples were collected from the outcrops. We took six 10-g subsamples from one 2-kg sample of slate (rock NH14-E, subsamples NH14-E1 through NH14-E6) and six from one visually homogeneous 2-kg sample of quartzite (M12-H1 through M12-H6). These subsamples were chosen more or less at random from three-dimensional grids along which the samples were sawed.

Ten-meter-scale compositional variations in visually uniform slate.—To determine the extent of heterogeneity within a "visually homogeneous" unit on a distance scale of ~ 10 m, we collected three more samples at the NH14 outcrop at ~10 m intervals (samples NH14-B,C,D). We also collected Carrabassett shale samples at ~ 10-m intervals from two outcrops (samples M15-A,D; samples M13-A,D, see below). The 10-m samples (~2 kg each) were sawed to yield 100 g subsamples that were subse-

TABLE 1

List of samples used in the experiments

Experiment	New Hampshire samples	Maine samples
1. Centimeter-scale compositional variation	NH14-E: six 10-g subsamples, NH14-E1 to E6, from a 2-kg, visually homogeneous outcrop of slate	M12-H: six 10-g subsamples, M12-H1 to H6, from a 2-kg, visually homogeneous qtz-rich metasediment
2. 10-m scale variations in homogeneous slate	NH14: three 100-g samples, NH14-B, C, and D	M15: four 100-g slate samples, M15-A and D taken 10 m apart, and 30 m away, samples M15-E and F, taken 1 m apart; also see M13 below
3. Compositional variations associated with graded beds	Not applicable	a. M12-F: five 10-g subsamples selected for variability in grain size (and thus proportion of quartz), M12-F-1 to F-5 b. M12-G: six 10-g subsamples taken at fixed intervals regardless of bedding-layer boundaries, M12-G1AS-1FS c. M12-A: one 100-g sample from a thick qtz-rich unit, M12-A2
4. Outcrop to outcrop compositional variation	NH15: four 100-g samples taken 10-15 m apart, NH15-A, B, D, E	a. M8: two 100-g samples several m apart, M8-B, C b. M11: four 100-g qtz-rich samples (M11-A, B, D, E), and one 100-g slate (M11-C) c. M13: two 100-g slate samples, M13-A, B, taken several m apart d. M15: four slate samples, M15-A and D taken 10 m apart, and 30 m away, Samples M15-E and F, taken 1 m apart
5. Outcrop at staurolite grade	NH3: five 10-g and two 100-g subsamples	Not applicable

quently crushed and powdered for analysis. Similar experiments could not reasonably be done at the other outcrops owing to their obvious heterogeneity.

Compositional variations associated with graded beds.—The face of Carrabassett outcrop M12 stands perpendicular to dozens of graded beds ranging in thickness from about one to tens of centimeters. Accordingly, we sampled it in more detail than we had done for the visually homogeneous Littleton outcrop. Two ~15 kg blocks (M12-F and M12-G), each composed of several graded beds, were sliced perpendicular to the bedding. To obtain extreme compositions for the graded beds, we subdivided the beds in sample M12-F into coarse and fine fractions

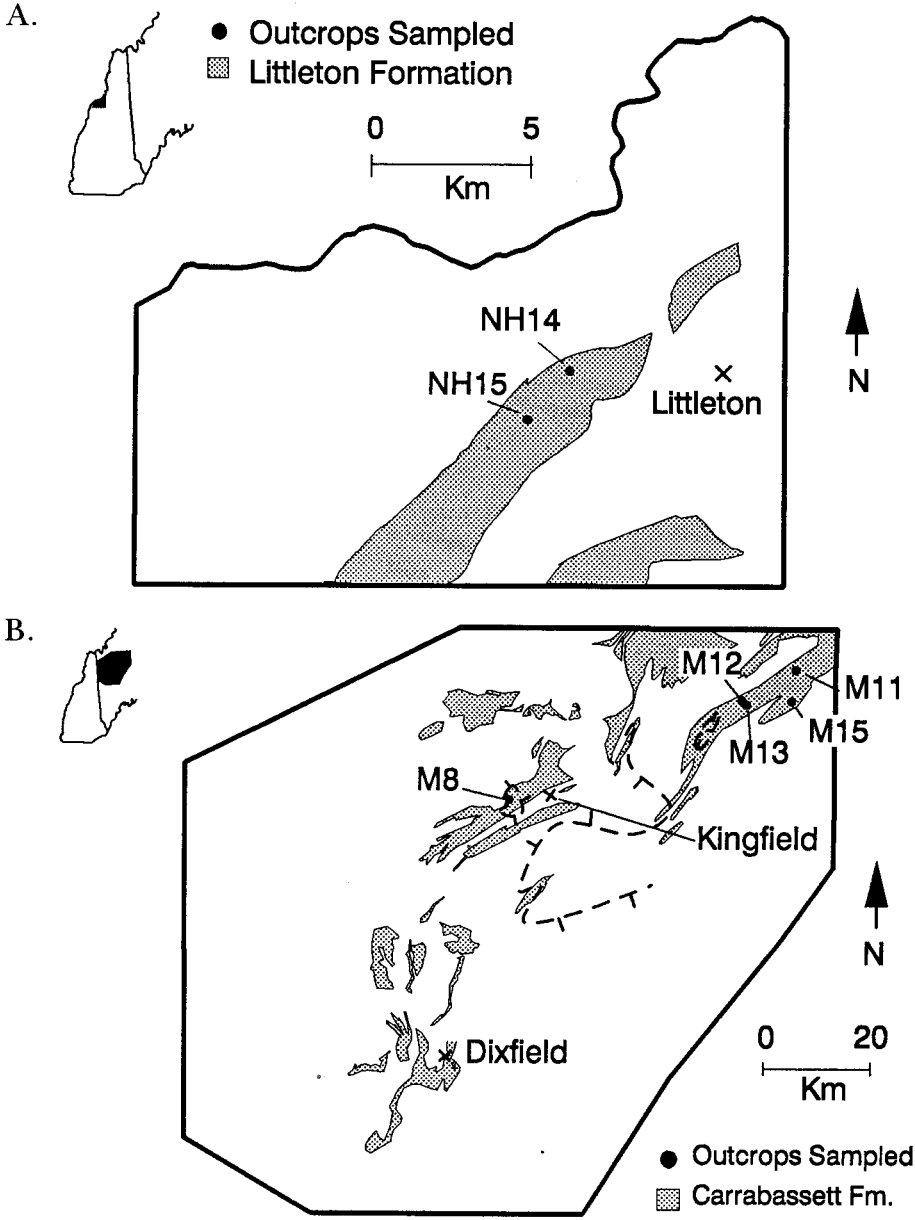

Fig. 1(A) Map showing distribution of Littleton Formation (hatched area) and outcrops of low-grade rocks sampled in western New Hampshire. The map is modified from Billings (1937) and Bothner (1991, personal communication). All Littleton outcrops in the area covered by the figure are in the chlorite zone. (B) Map showing distribution of Carrabassett Formation and outcrops of low-grade rocks sampled in western Maine. The map is modified from Moench and Pankiwskyj (1988). Dashed lines represent the staurolite-in isograd; tick marks are on the high-grade side. One low-grade outcrop is surrounded by staurolite zone rocks west of Kingfield, and one staurolite area southwest of outcrop M12 is surrounded by low-grade rocks. High-grade rocks occur in the west and south portions of the map, but the exact position of isograd is not shown.

(bottoms and tops of beds) that could be separated from each other by sawing. This yielded small subsamples of ~10 g each (M12-F1 through M12-F5). Graded beds in M12-G were sampled using a different strategy. Subsamples were taken at ~3 cm intervals regardless of grain size or possible boundaries between layers; this yielded six subsamples on the order of 10 g each (M12-G 1AS-1FS). Finally, we prepared a 100 g subsample of a massive quartzite (M12-A) obtained within an outcrop of graded beds.

Outcrop-to-outcrop compositional variations.—To get some idea of variability from outcrop to outcrop, we analyzed 100-g samples from several other outcrops of low-grade rocks (NH15, M8, M11, M13, M15; see fig. 1 for locations) to compare their compositions with those at the Slate Ledge (NH14) and Kingsbury localities (M12). Collection schemes varied at each outcrop depending on the exposure and the lithologies present. At outcrop NH15, which contains graded beds of variable thickness, several samples were selected at intervals ranging from 5 to 10 m. At outcrop M8, which consists of two small exposures of homogeneous slate, two samples were selected several tens of meters apart. Outcrop M11 was 1.5 m across and consisted of alternating layers of massive quartzite (~20 cm thick) and very thin slate (~2 cm thick). There, four quartzite samples (M11-A,B,D,E) and one sample from a thin slate layer (M11-C) were taken. Two samples of visually homogeneous slates were taken from locations separated by several meters in outcrop M13 (M13-A,B). Outcrop M15 consists mostly of massive slate containing some very thin graded beds. Four samples from this outcrop were analyzed: two collected 10 m apart (M15-A and M15-D) and two others collected 30 m away from M15-D and taken 1 m apart and perpendicular to the observed bedding (M15-E and M15-F). Most of the these samples were ~2 kg hand-specimens selected at various intervals from different outcrops. In the laboratory, ~100 g slabs were sawed from each and prepared for analysis.

Similar suites of samples of medium- and high-grade rocks were also collected but have not yet been analyzed. We obtained preliminary data, however, for subsamples from one hand specimen taken from an outcrop of medium-grade staurolite schist (NH3, in SW New Hampshire), in order to search for small-scale interelement trends resulting from metamorphism.

Sample preparation and analysis.—Saw marks were removed from the surfaces of all blocks by use of a diamond-impregnated grinding wheel. The blocks were then washed twice with distilled water in an ultrasonic bath for 5 min at a time. After they had dried, all samples were crushed to fragments <5 mm across in a stainless steel mortar. Finally, each sample was powdered in a Spex shatterbox using an alumina ceramic grinding vessel. For actual INAA analysis, aliquots of powder weighing between 140 and 260 mg were used; thus, analysis of a "10-g" sample, as used below, means analysis of powdered material representing 10 g of powdered sample. Similarly, duplicate glass discs each containing 0.4 g of

powder were used for major-element analysis and ~4 g of powder was compressed into pellets for each XRF trace-element analysis.

Major-element data were obtained by XRF. Sample preparation and methods for the XRF major-element analyses are described by Couture and others (1993). Analyses for Zr were done by INAA and XRF. Sample preparation and standard analyses for INAA are described by Korotev (1987a,b). The INAA procedure used for the Littleton samples has been described by Korotev (1991), except that samples were irradiated for 12 h at a neutron flux of 4.0×10^{13} neutrons/cm^2/s. XRF trace-element sample preparation and analysis are described by Couture and others (1993) and Couture and Dymek (1995). Relative analytical uncertainties are given in table 2.

ANALYTICAL RESULTS

Centimeter-scale Compositional Variations; the 10-g Subsample Experiments

The compositions of the 10-g subsamples of Littleton slate and Carrabassett quartzite (NH14-E1 through E6 and M12-H1 through H6)

TABLE 2

Analytical results and statistics for NH14-E and M12-H ~10g subsamples (wt%, except Zr, ppm)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3t	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	SUM	Zr
NH14-E1	61.7	0.93	17.1	7.93	0.09	2.85	0.34	1.54	3.25	0.13	4.0	99.82	181
NH14-E2	58.5	1.01	18.7	8.39	0.08	3.24	0.35	1.49	3.62	0.16	4.24	99.78	182
NH14-E3	58.8	1.02	18.8	8.1	0.07	3.10	0.30	1.58	3.68	0.13	4.24	99.82	192
NH14-E4	58.3	1.01	19.1	8.29	0.09	3.24	0.20	1.51	3.77	0.17	4.19	99.87	190
NH14-E5	58.7	1.04	19.1	8.34	0.08	3.21	0.25	1.48	3.75	0.13	4.22	100.3	193
NH14-E6	60.7	0.93	16.9	8.61	0.08	2.66	0.39	1.48	3.36	0.14	4.40	99.65	189
M12-H1	88.3	0.45	5.1	2.7	0.12	0.74	0.48	1.06	0.09	0.09	0.85	99.98	347
M12-H2	88.3	0.41	5.2	2.83	0.11	0.81	0.46	1.00	0.09	0.08	0.89	100.18	275
M12-H3	88.3	0.46	4.9	3.09	0.11	0.84	0.37	0.85	0.11	0.06	0.96	100.05	378
M12-H4	86.9	0.40	4.9	4.22	0.09	1.27	0.27	0.65	0.23	0.07	1.16	100.16	258
M12-H5	85.9	0.40	5.3	4.46	0.09	1.36	0.24	0.68	0.19	0.01	1.34	99.97	276
M12-H6	88.8	0.35	4.5	3.02	0.11	0.89	0.40	0.75	0.09	0.10	0.95	99.96	244
Analytical uncertainties (% relative)													
NH14	1	2	1	1	5	2	3	1	1	10	1		5
M12	1	3	1	1	5	5	3	1	6	30	1		5
NH14-E, LOI-free basis:													
Avg	62.1	1.03	19.1	8.64	0.08	3.19	0.32	1.58	3.73	0.15			196
s	1.4	0.05	1.0	0.26	0.01	0.30	0.07	0.04	0.23	0.02			5
s_m	0.6	0.00	0.4	0.11	0.00	0.10	0.03	0.02	0.09	0.01			2
M12-H, LOI-free basis:													
Avg	88.7	0.42	5.02	3.4	0.11	1.00	0.37	0.84	0.14	0.07			299
s	1.0	0.04	0.30	0.8	0.01	0.30	0.10	0.17	0.06	0.03			54
s_m	0.4	0.02	0.11	0.3	0.00	0.11	0.04	0.07	0.02	0.01			22
estimated mass (g) to obtain 5% sample std dev													
NH14-E	4.2	18	24	7.1	60	50	400	5	29	97			
M12-H	1.0	69	23	400	90	570	530	325	1600	1500			

Avg = sample average; s = sample standard deviation; s_m = standard deviation of the mean.

are listed in table 2. The extents of compositional variation are illustrated graphically (on an LOI-free basis) in figure 2.

Based on the F-test, variances for all elements in the 10-g subsamples except P_2O_5 in the NH14-E slate and SiO_2 in the M12-H quartzite significantly exceed analytical uncertainty (95 percent confidence level), demonstrating actual compositional variability. For Al_2O_3 and K_2O, variances among NH14-E subsamples exceed those of M12-H subsamples (90 percent confidence level). For FeO, Na_2O, LOI, and Zr, variances among M12-H subsamples exceed those of NH14-E subsamples. For the other major elements, variations in concentrations among the 10-g quartzite subsamples are about the same as those for the slate subsamples.

Ten-meter scale Compositional Variations within a Visually Homogeneous Outcrop

Data for three ~100 g samples from the NH14 outcrop are given in table 3. Figure 2E compares the compositional variation for four ~100 g samples to that for the six 10-g subsamples. (The fourth ~100-g sample is the mean value for the six 10-g subsamples, as if they had been

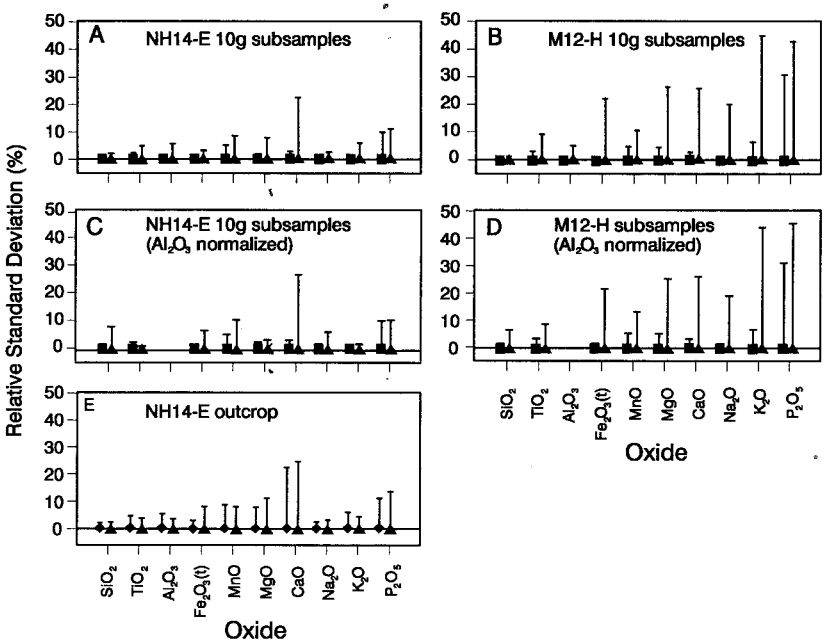

Fig. 2. Variations in major-element concentrations (triangles) are shown as error bars that represent one relative standard deviation (1 sample standard deviation × 100/avg value). Analytical uncertainties (squares) are also shown as $\pm 1\sigma$ converted to percent. (A) Six 10-g Slate Ledge (NH14-E) subsamples; (B) Six 10-g M12-H subsamples; (C,D) Variations in Al_2O_3-normalized major-element concentrations of the six NH14-E and Kingsbury (M12-H) subsamples; (E) Variations of the six 10-g subsamples (diamonds) from the NH14-E slate are compared with those of the four NH14 100-g outcrop samples (squares).

TABLE 3

Compositions of Littleton-Carrabassett 100-g outcrop samples (wt%, except Zr, ppm)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3t	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	SUM	Zr
NH14-B	63.6	0.92	17.0	7.09	0.07	2.54	0.21	1.63	3.26	0.17	3.4	99.89	207
NH14-C	62.4	0.98	17.5	7.03	0.07	2.35	0.25	1.54	3.46	0.16	3.8	99.58	238
NH14-D	61.1	1.00	18.1	7.73	0.07	2.85	0.17	1.63	3.41	0.12	3.6	99.79	200
NH15-A	86.2	0.85	6.2	3.33	0.03	0.38	0.03	0.14	0.78	0.06	1.8	99.80	1340
NH15-B	67.1	1.01	16.8	6.49	0.03	0.82	0.02	0.27	3.65	0.11	3.9	100.20	290
NH15-D	86.3	0.77	6.3	3.24	0.02	0.36	0.06	0.42	0.93	0.06	1.3	99.76	1200
NH15-E	77.8	0.76	11.0	4.82	0.03	0.54	0.06	0.66	1.87	0.06	2.4	100.00	421
M8-B	82.4	0.57	8.2	4.02	0.04	0.63	0.10	1.07	1.16	0.07	1.6	99.86	332
M8-C	74.8	0.82	11.6	5.62	0.06	0.97	0.15	0.89	1.88	0.12	2.3	99.21	279
M11-A	74.4	0.84	13.0	4.36	0.05	0.87	0.24	1.68	2.09	0.11	2.1	99.74	300
M11-B	80.0	0.65	9.5	4.78	0.05	0.86	0.16	0.84	1.39	0.09	1.8	100.12	358
M11-C	58.2	1.07	19.4	8.85	0.11	3.05	0.38	1.09	3.84	0.17	3.8	99.96	190
M11-D	75.5	0.75	11.7	4.89	0.06	0.95	0.20	1.30	1.82	0.12	2.3	99.59	243
M11-E	80.8	0.62	9.1	4.46	0.05	0.76	0.29	0.49	1.26	0.10	1.8	99.73	314
M12-A2	87.4	0.43	5.3	4.03	0.06	0.37	0.47	0.35	0.52	0.06	0.8	99.84	285
M13-A	60.2	1.06	20.3	7.82	0.08	1.38	0.19	1.11	3.83	0.16	3.6	99.73	230
M13-B	61.1	1.06	19.8	7.78	0.08	1.43	0.19	0.97	3.76	0.14	3.5	99.81	200
M15-A	59.2	1.03	20.5	8.18	0.13	1.85	0.18	0.90	4.25	0.16	3.7	100.08	160
M15-D	50.2	1.21	23.1	9.84	0.17	3.31	1.24	1.48	4.18	0.61	4.7	100.04	170
M15-E	52.2	1.10	24.9	8.85	0.10	1.84	0.23	0.75	5.37	0.20	4.7	100.24	154
M15-F	71.5	0.95	14.1	5.40	0.06	1.08	0.11	1.01	2.71	0.09	2.4	99.41	260
Average outcrop compositions, LOI-free basis:													
NH-14	64.1	1.01	18.4	7.83	0.08	2.80	0.24	1.54	3.56	0.15			
NH-15	81.2	0.87	10.4	4.59	0.03	0.54	0.04	0.31	1.86	0.07			
M8	80.2	0.71	10.1	4.92	0.05	0.82	0.13	0.91	1.55	0.10			
M11	75.5	0.81	12.9	5.62	0.06	1.34	0.28	1.11	2.14	0.12			
M12	82.5	0.62	9.3	5.03	0.10	1.33	0.42	0.80	1.33	0.09			
M13	62.9	1.10	20.7	8.09	0.08	1.46	0.19	0.93	3.93	0.15			
M15	60.6	1.12	21.5	8.41	0.12	2.11	0.46	0.97	4.30	0.28			
Avg	72	0.89	15	6.4	0.07	1.5	0.25	0.9	2.7	0.14			
s	10	0.19	5	1.7	0.03	0.8	0.15	0.4	1.2	0.07			
s(%)	13	21	36	26	43	52	60	39	46	50			

Avg = average for all outcrops; s = sample standard deviation for average of all outcrops; s(%) = s × 100/mean.

analyzed collectively as a single, 60 g sample.) If the average compositions and standard deviations found for the 10 g samples were truly representative of the outcrop, we would expect the sample standard deviation for 100 g samples to be as small as the standard deviation of the mean for the ten 10 g subsamples. In fact, the sample standard deviations among the 100 g samples are about the same as those for the 10 g subsamples; this is further discussed below.

Compositional Variations Associated with Graded Beds

Given that turbidite beds are still evident in some outcrops of low-grade rocks, we may expect substantial compositional variations arising from differences in sedimentary mineral proportions even on a

sample size scale of several kilograms. Obvious heterogeneities caused by cyclical graded beds are visible in portions of the M12 quartzite outcrop. Samples should range from quartz-rich to quartz-poor (clay-rich), leading to a substantial compositional range for all elements (high-SiO_2 in quartz-rich samples, with a corresponding reduction in concentration for most elements as the presence of quartz reduces the proportion of clay). Data for SiO_2 and Al_2O_3 in eleven 10 g samples from the M12 outcrop are included in table 4 and from one 100 g sample in table 3; figure 3A reflects the range of compositions sampled. Compositions of samples M12-F, 1-5, correlate qualitatively with visually observed grain size, as expected for mixtures of quartz and fine-grained clay in different proportions.

It is unlikely that the average composition of the M12-H samples (from a visually homogeneous portion of the outcrop) is the exact average for the entire M12 outcrop. Even so, because it is visually homogeneous, we can safely conclude that the average composition of this quartzite outcrop (M12) differs substantially from that of the pelite outcrop (NH14). This conclusion is easily reached without chemical analysis on the basis of the different rock types. In outcrops of higher metamorphic grade, however, such obvious differences may be masked by recrystallization and especially deformation, so that a higher SiO_2 concentration such as that in M12 could be attributed to Si gain, or a lower SiO_2 concentration such as that in NH14 could be attributed to Si loss. Consequently, knowledge of differences and variations in chemical compositions may be the best way to identify the nature of the local protolith and determine whether its composition has changed as a consequence of long-range element mobility during metamorphism. Otherwise, a higher-grade rock derived from a quartz-rich sediment might be mistaken for a metamorphosed pelite that had gained silica.

Outcrop-to-Outcrop Compositional Variations

Inspection of table 2 shows that chemical compositions can differ significantly from outcrop to outcrop, even though we cannot easily determine the average composition of a particular outcrop. It is not clear

TABLE 4

Compositions of additional Carrabassett 10-g samples (wt%, except Zr, ppm)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3t	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	SUM	Zr
M12-F1	51.0	1.29	24.3	8.79	0.10	2.81	0.32	1.48	5.12	0.15	4.2	99.59	222
M12-F2	70.7	0.72	13.2	6.38	0.06	2.03	0.35	1.34	2.72	0.15	2.0	99.68	196
M12-F3	53.2	1.20	23.4	8.33	0.10	2.77	0.34	1.50	4.85	0.16	4.0	99.85	218
M12-F4	75.1	0.69	10.9	5.71	0.06	1.75	0.36	1.15	2.33	0.17	1.6	99.78	361
M12-F5	56.3	1.12	21.1	8.42	0.09	2.75	0.35	1.54	4.23	0.15	3.7	99.76	222
M12-G1AS	58.4	1.07	19.1	8.80	0.09	3.02	0.35	1.13	3.70	0.15	3.7	99.49	178
M12-G1BS	60.2	1.00	19.0	7.61	0.09	2.55	0.45	1.73	3.72	0.13	3.2	99.66	211
M12-G1CS	59.6	1.06	19.6	7.56	0.09	2.27	0.38	1.34	4.08	0.19	3.5	99.71	208
M12-G1DS	75.4	0.64	10.5	5.54	0.07	1.57	0.28	1.07	2.37	0.09	1.6	99.14	237
M12-G1ES	60.4	1.05	19.5	7.66	0.10	2.50	0.41	1.37	4.06	0.13	3.3	100.44	215
M12-G1FS	61.1	1.01	18.8	7.35	0.11	2.37	0.37	1.16	4.02	0.15	3.3	99.77	140

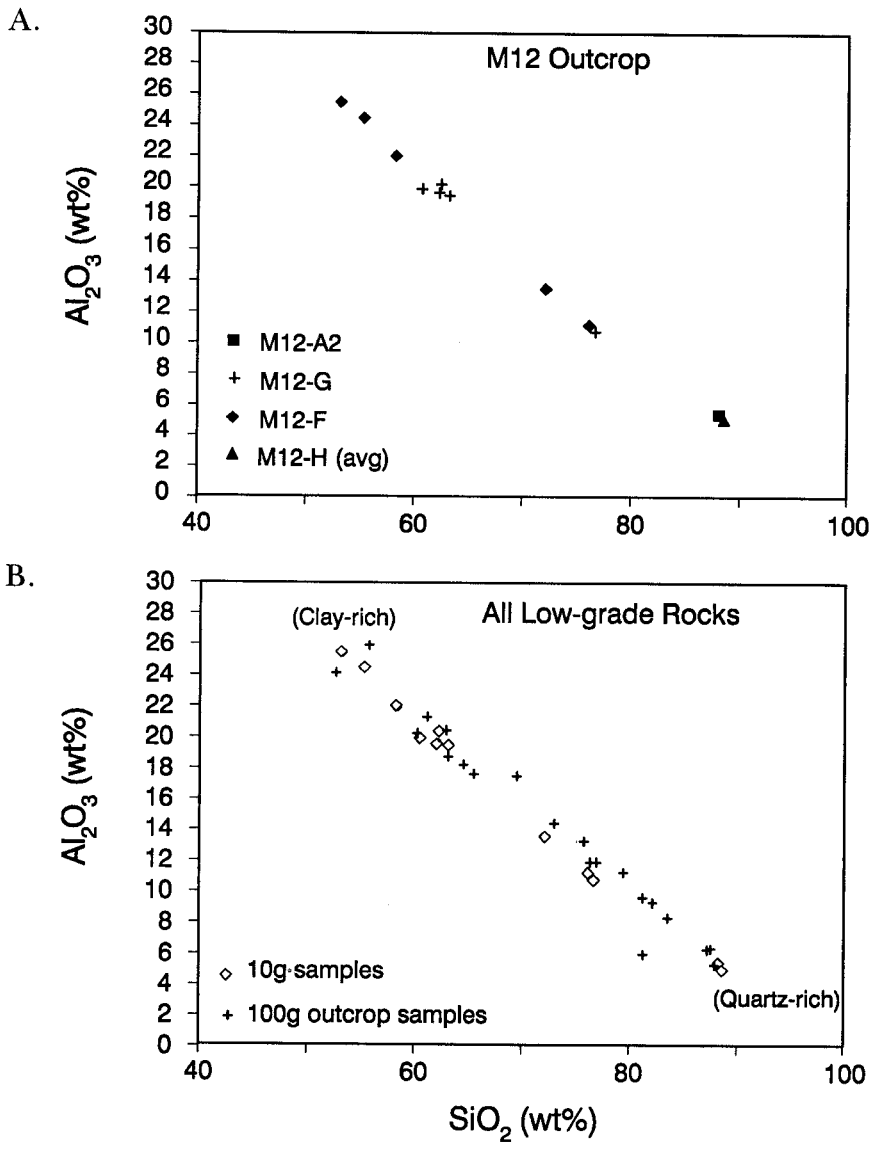

Fig. 3(A) Concentrations of Al_2O_3 are plotted against those for SiO_2 for eleven 10-g samples and one 100-g sample from the M12 meta-turbidite outcrop. (B) Concentrations of Al_2O_3 are plotted against those for SiO_2 for samples from each of seven Littleton-Carrabassett outcrops. The compositional range for 10-g samples essentially matches that of the M12 outcrop.

that such differences in chemical composition would average out region by region (that is, distance scales of hundreds of meters to kilometers). This makes it difficult to show whether a population of higher-grade rocks came from the same average protolith as unmetamorphosed or low-grade rocks, a demonstration that is essential to consideration 2 discussed in the introduction. Protolith heterogeneities on all distance scales must somehow be taken into account when samples of one metamorphic grade are compared with samples from another.

Compositions of seventeen 100-g samples from other Littleton-Carrabassett outcrops of low metamorphic grade are included in table 3, and averages of values for the seven low-grade outcrops whose locations are shown in figure 1 are also given in table 3. The range of composition in 100-g samples from all seven outcrops is shown in figure 3B, and it is evident that their compositions span essentially the same range as that found for the 10-g samples from the M12 outcrop (fig. 3A).

DISCUSSION

In the previous sections, we presented a series of analyses based on an experimental design to determine the magnitude and extent of compositional variations in rocks of the Littleton-Carrabassett Formation. Our results reveal significant compositional heterogeneity at every size scale of sample investigated. In the following sections, we explore some consequences of our new data in order to address a number of related issues:

We use the results from our subsample experiment to estimate a sample size we would need to use in order to obtain compositions truly representative of a particular outcrop. We show that these estimates are misleading. We describe an example of the kind of interelement correlations that result from variations in proportions of sedimentary minerals. We quantify the nature and proportions of the principal sedimentary mineral components in the protoliths of the Littleton-Carrabassett rocks through the use of a mixing model. This approach aids in understanding the causes of compositional variability on the several size scales represented in our data set. In particular, it enables distinction between compositional variability caused by differences in abundances of sedimentary mineral components as opposed to differences possibly induced by metamorphism. We thus test our working hypothesis, stated in the introduction, that low-grade rocks retain compositional variations of their sedimentary protoliths, including effects of diagenesis, with minimal modification by metamorphic element transport on distance scales of centimeters or greater. Lastly, as a contrast to the rest of our results, we present an example demonstrating that, under appropriate circumstances, real metamorphic element mobility can be observed at the centimeter distance scale.

What Might Constitute a Representative Sample of Visually Homogeneous Slate?

In principle, compositional variations among each set of six subsamples allow us to estimate roughly the sample mass that would be

necessary to yield values for each element close to the true population average value (for example, within a sample standard deviation of 5 percent), that is, a sample mass large enough to avoid a significant "sampling problem." We then compare those estimates with results based on analyzed compositions of the 100-g samples from the same outcrops.

The relationship we used for these estimates is $s_m = s/(n^{0.5})$, where s_m is the standard deviation of the mean, s is the sample standard deviation for the six 10 g subsamples, and n is the number of subsamples. For the calculations, we used the values of s from table 2, set s_m equal to 5 percent of the mean concentration for each element, and solved for n (Walpole and Myers, 1985). In this exercise, n is, in effect, the number of 10 g blocks that must be combined to reach the required level of certainty with a single analysis.

According to these estimates (table 2), for most elements, a 100 g sample of NH14-E would be more than adequate to provide values within 5 percent of the "true" value with ~95 percent confidence (~2s). For M12-H, this estimate suggests that substantially larger samples (up to ~2 kg) would be needed to provide values within 5 percent of the "true" value with ~95 percent (2s) confidence for K_2O and P_2O_5. We note that the required sample mass would surely be much larger in higher-grade rocks, because those may contain porphyroblasts that range in size up to several centimeters (Billings, 1956; Guidotti, 1989). These estimates presume that the sample variations have normal distributions, but in reality many do not. For example, SiO_2, TiO_2, Al_2O_3, and MnO in the NH14-E subsamples and K_2O in M12-H subsamples fail a Shapiro-Wilks test for normality with 95 percent certainty (Shapiro and Wilks, 1965).

For samples from an outcrop whose compositional characteristics were uniformly those found for the 10 g samples (that is, the same average compositions and standard deviations), we would expect that the sample standard deviation uncertainty for a set of 100-g samples would roughly equal the standard deviation of the mean value for ten 10-g subsamples. We observe (fig. 2), however, that for some oxides, the sample standard deviations for the four 100-g samples are larger than that prediction, in fact, about as large as or larger than the sample standard deviations for the six 10-g subsamples. This indicates that the NH14 outcrop cannot be viewed as consisting of a population of 10-g blocks with the same compositional variations as the NH14-E 10-g subsamples. Instead, there are larger scale (tens of meters) heterogeneities within the visually homogeneous outcrop. This exercise shows that our estimates of the single sample mass required to obtain 5 percent accuracy for a 100-g sample and, based on the variance of the 10-g subsamples, are not valid as sample masses required to obtain a correct average composition of even a visually homogeneous outcrop (which is a two-dimensional unit of arbitrary and accidental size, anyway) or of Littleton-Carrabassett low-grade rocks generally. *Because there are heterogeneities on different scales, it is inaccurate to regard kilogram-sized samples even*

of lowest metamorphic grade as if they adequately represented a single compositional population that can be characterized easily by a few analyses.

Metamorphic and Sedimentary Compositional Trends

Constraints from major elements.—How can we distinguish between compositional variations within the sedimentary protolith and compositional variations produced by metamorphic gain or loss of an element? Consider SiO_2, for which large-scale mobilization and loss has been argued (Ague, 1991) and Al_2O_3, sometimes considered immobile during metamorphism (Ferry, 1982). In a sedimentary system in which the main components are quartz and clay minerals, concentrations of SiO_2 correlate negatively with those of Al_2O_3 and most other elements. This occurs because quartz is nearly pure SiO_2, whereas Al_2O_3 and most other elements are associated with clays, and the bulk system consists mainly of mixtures of quartz and clays. This negative correlation is shown in figure 3 for Littleton-Carrabassett low-grade rocks. The data plot along a single, well-defined trend, whose width averages about ±5 percent SiO_2. As discussed below, this trend can be ascribed to mixing of sedimentary components. Because one endmember of the trend is essentially pure SiO_2 (quartz), however, gain or loss of SiO_2 during metamorphism would produce an identical trend.

Figure 4A includes data for medium- and high-grade Littleton rocks. It is our intention eventually to characterize our collection of medium- and high-grade rocks in the same detail as we have done here for the low-grade rocks. In lieu of such detailed data, we use results from higher-grade Littleton pelites presented by Moss and others (1995). The medium- and high-grade sample data lie along the same trend as the data for the low-grade rocks. An idea of the amount of gain or loss of SiO_2 required to account for the length of the trend is shown in figure 4B, which takes as its starting point an arbitrary composition (~70 wt percent SiO_2) in the center of the sample field. Note from figure 4A that the medium- and high-grade samples do not appreciably extend the line in either direction beyond the range for the low-grade samples. Values for several high-grade, 2-kg samples plot at the low-SiO_2 end of the distribution, however, whereas the only values for low-grade rocks that plot there are from 10-g subsamples. We might thus be tempted to argue that this asymmetry is evidence for substantial SiO_2 loss for at least some high-grade rocke. Such evidence for loss of SiO_2 is nevertheless ambiguous; it depends on the assumptions that the samples analyzed properly represent the different metamorphic grades and that the average protolith for the higher-grade samples was not more quartz-poor than that for the low-grade samples. These low-silica, high-grade rocks could just as easily represent isochemically metamorphosed equivalents of the low-silica, 10 g subsamples.

Constraints from trace elements.—Trace elements can help us distinguish between compositions corresponding to protolith characteristics and those resulting from metamorphic redistribution. Figure 5 shows the

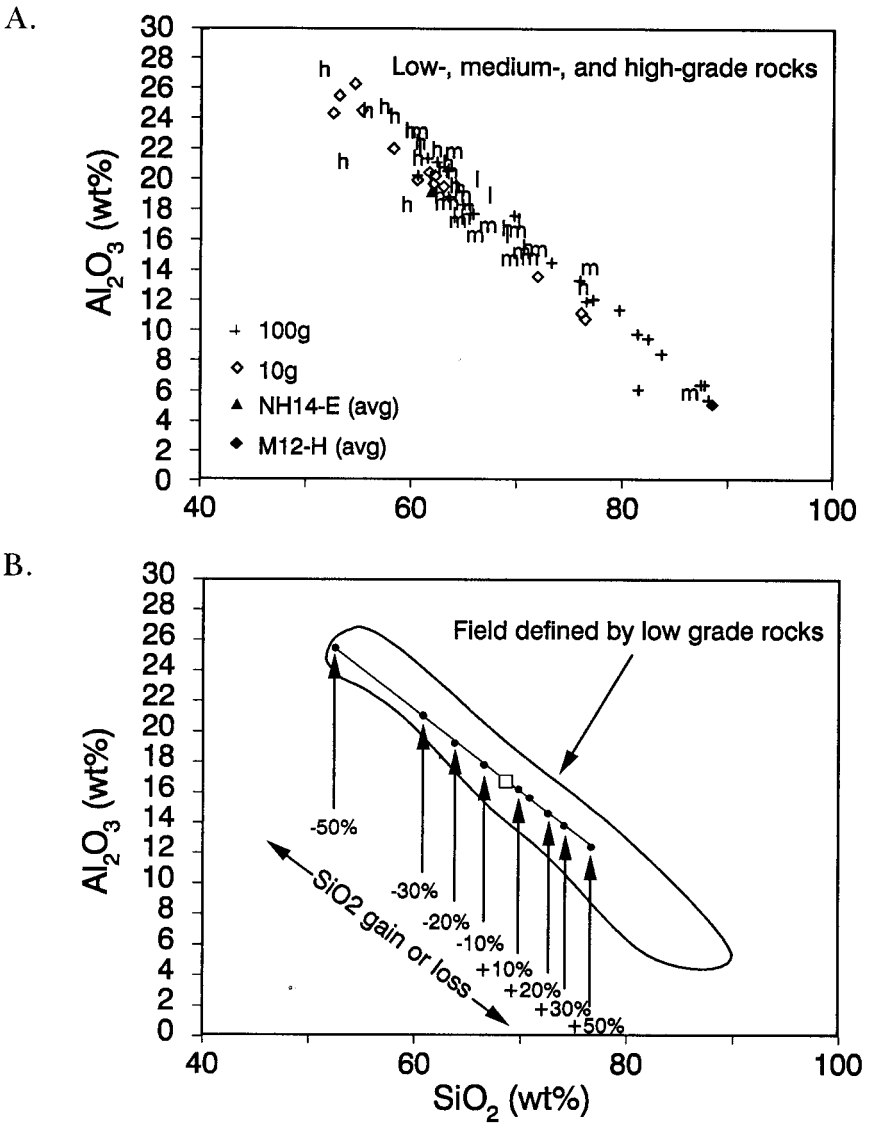

Fig. 4(A) Concentrations of Al_2O_3 and SiO_2 are plotted for the 10 g and 100 g Littleton-Carrabassett subsamples (this study) and for the Littleton 2-kg hand specimens analyzed by Moss and others (1995), which include all three metamorphic grades (l = low grade, m = medium grade, and h = high grade). (B) Changes in composition that major-element mobility during metamorphism can produce are shown on a SiO_2-Al_2O_3 diagram. Theoretical results were calculated starting with a point in the middle of the field; lines of similar character would occur for other starting compositions. The field defined by low-grade rocks plotted in (A) is shown for comparison.

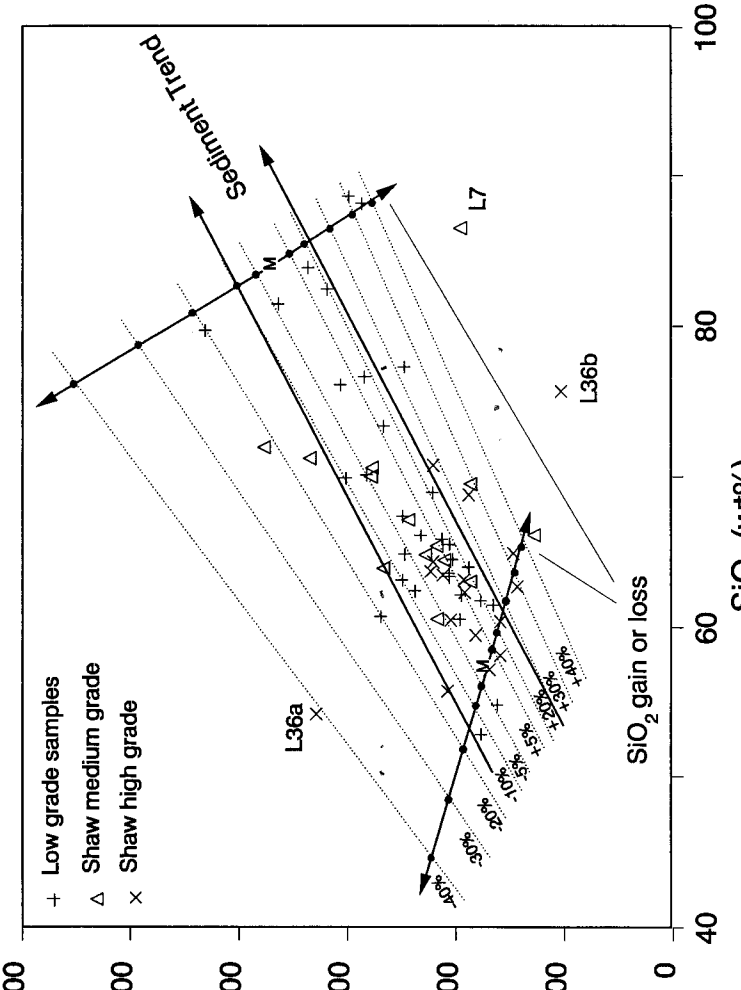

Fig. 5. Concentrations of Zr and SiO_2 are plotted for all Littleton-Carrabassett rocks from this study and that of Moss and others (1995). Low-grade rocks include all 100 g samples analyzed in this work, low-grade rocks analyzed by Moss and others (1995), and average compositions for M12-F, M12-G, M12-H, and NH14-E. The low-grade rocks show a rough positive correlation between Zr and SiO_2 concentrations, presumably caused by partial association of zircon with quartz during sedimentary sorting in the protolith. The "most likely" low-grade field (27 out of 32 low-grade rocks) is defined as the region between the long arrows. Double-ended arrows that extrapolate to 0 and 100 percent SiO_2 show the paths of pure SiO_2 gain or loss from points M, two points from the middle of the "most likely" low-grade field and near the extremes of observed SiO_2 concentration. The dashed lines show approximately equal values of SiO_2 gain or loss. Data for higher-grade samples plot in the same field as those for low-grade samples, and no systematic mobility of SiO_2 into or out of the higher-grade rocks is evident. (See text for discussion of outlying points.)

correlation between SiO_2 and Zr for low-grade samples from the Littleton and Carrabassett Formations. We would expect and we observe a rough, positive correlation between SiO_2 and Zr because most of the Zr is in zircon, which follows quartz rather than clay during sedimentation. The correlation should not be a perfect one, and it is not; scatter should arise from partial separation of zircon from quartz during sedimentary sorting, zircon being almost twice as dense as quartz. Two extreme points for quartz-rich sediments (not included in fig. 5) emphasize this: NH15-A, SiO_2 = 87.8 percent and Zr = 1360 ppm; and NH15-D, SiO_2 = 87.5 percent and Zr = 1220 ppm. We have outlined on figure 5 a range of probable protolith values that contains 27 of the 32 points for low-grade samples (labeled "sediment trend").

Zircon is stable even under rather severe conditions of metamorphism so we would not expect Zr to follow SiO_2 during metamorphic mobilization of silica, if such mobilization occurred. Thus, a metamorphic trend would lie at steep angles to the sediment trend, as shown by the double arrows in figure 5. Also shown in figure 5 is the fraction of the original SiO_2 in a sample that must be gained or lost to move the point for that sample a given distance from the middle of the protolith field. Figure 5 includes data for medium- and high-grade Littleton rocks (Moss and others, 1995). Most of those values plot within the range defined by the low-grade samples and believed to be the protolith trend. The scatter of data for the higher-grade samples is somewhat greater, however, so that the fraction that plots within the trend is smaller than that of the low-grade samples. The scatter is in the directions of both SiO_2 loss and SiO_2 gain. This may reflect more extensive separation of zircon from quartz in the portions of the protolith from which the higher-grade samples derived, redistribution of SiO_2 during metamorphism, or a different protolith altogether.

Data for two high-grade samples (L36 a and b, Moss and others, 1995) plot well away from the sediment trend. These are portions of dark and light bands from the same gneiss, where metamorphic separation clearly has occurred. One medium-grade sample, (L7), also stands out. It may have derived from an unusually Zr-poor, quartz-rich portion of the protolith, or, alternatively, it may have gained >50 percent SiO_2 relative to the average for the SiO_2-Zr trend.

The field occupied by the low-grade samples is wide enough that a rock whose initial composition was in its middle could lose or gain ~ 20 percent SiO_2 and still plot within it. Because of this breadth, some gain or loss of SiO_2 for individual higher-grade samples could be obscured. Nonetheless, it is important that the data for higher-grade samples do not lie systematically or mainly on the low or the high side of the low-grade distribution, as we would expect if systematic net gain of SiO_2 by (or loss of it from) the Littleton-Carrabassett pelites had occurred during metamorphism. Overall, the higher-grade Littleton-Carrabassett rocks appear to retain the Zr and SiO_2 distribution characteristics of the

TABLE 5

Composition of LOI-free mixing model components

mix com	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
MC	56.7	1.85	22.0	9.15	0.65	2.00	2.19	4.70	0.33	0.43
MCH	27.1	0.00	22.8	35.4	0.04	13.2	0.00	0.01	1.50	0.02
NHC	56.9	1.44	23.9	7.84	0.11	2.00	0.42	2.22	5.00	0.20
NHCH	28.6	0.00	22.7	27.6	0.05	19.5	0.01	0.01	1.50	0.02
QTZ	100.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PYR	0.00	0.00	0.00	45.0	0.00	0.00	0.00	0.00	0.00	0.00
ILM	0.00	50.1	0.00	49.9	0.00	0.00	0.00	0.00	0.00	0.00

Molecular formulas for mixing components

MC: $[Ca_{0.15}Na_{0.57}K_{0.03}](Mg_{0.19}Fe_{0.43}Ti_{0.09}Mn_{0.03}P_{0.02}Al_{1.18})(Si_{3.55}Al_{0.45})O_{10}(OH)_2$

MCH: $(K_{0.19}Mg_{1.92}Fe_{2.61}Mn_{0.0}Al_{1.28})(Si_{2.65}Al_{1.35})O_{10}(OH)_8$

NHC: $[Ca_{0.03}Na_{0.27}K_{0.40}](Mg_{0.19}Fe_{0.37}Ti_{0.07}Mn_{0.01}P_{0.01}Al_{1.33})(Si_{3.57}Al_{0.43})O_{10}(OH)_2$

NHCH: $(K_{0.18}Mg_{2.71}Fe_{1.94}Mn_{0.0}Al_{1.16})(Si_{2.67}Al_{1.33})O_{10}(OH)_8$

Model results for NH14-E samples

samp\mix com	NHC	QTZ	NHCL	PYR	sum
NH14-E1	66.7	23.9	8.4	1.6	100.6
NH14-E2	72.3	17.2	10.0	0.7	100.2
NH14-E3	73.6	17.0	9.0	0.5	100.1
NH14-E4	74.3	15.9	9.7	0.3	100.2
NH14-E5	74.4	16.1	9.6	0.5	100.7
NH14-E6	67.0	23.3	7.3	3.9	101.5

Goodness of fit (number of samples with absolute relative uncertainty)

	<1%	1-2%	2-5%	5-10%	10-20%	20-50%	>50%
NHC	6	0	0	0	0	0	0
QTZ	5	1	0	0	0	0	0
NHCL	0	2	4	0	0	0	0
PYR	0	0	0	1	3	1	1
Sum	6	0	0	0	0	0	0
SiO_2	|6|	0	0	0	0	0	0
TiO_2	5	|1|	0	0	0	0	0
Al_2O_3	|6|	0	0	0	0	0	0
Fe_2O_3	|6|	0	0	0	0	0	0
MnO	0	0	1	|3|	2	0	0
MgO	6	|0|	0	0	0	0	0
CaO	1	0	|0|	0	1	4	0
Na_2O	|1|	0	3	2	0	0	0
K_2O	|2|	4	0	0	0	0	0
P_2O_5	1	0	1	|2|	2	0	0

\| \| Vertical lines represent average analytical uncertainty.

TABLE 5

Model results for M12-H subsamples using NH mixing components (Continued)

samp\mix com	NHC	QTZ	NHCL	ILM	sum
M12-H1	18.3	77.7	3.1	0.6	99.7
M12-H2	17.9	77.8	3.7	0.6	100.0
M12-H3	16.1	78.8	4.4	0.9	100.2
M12-H4	13.0	78.2	8.1	1.2	100.5
M12-H5	14.0	76.7	8.6	1.2	100.5
M12-H6	14.2	80.2	4.9	0.7	100.0

	<1%	1-2%	2-5%	5-10%	10-20%	20-50%	>50%
NHC	0	0	0	0	4	2	0
QTZ	0	6	0	0	0	0	0
NHCL	0	0	0	0	0	4	2
ILM	0	0	0	0	0	0	6
SUM	0	0	6	0	0	0	0
SiO_2	|6|	0	0	0	0	0	0
TiO_2	0	0	|0|	0	0	6	0
Al_2O_3	|0|	0	0	6	0	0	0
Fe_2O_3	|0|	0	0	6	0	0	0
MnO	0	0	|0|	0	0	0	6
MgO	0	0	0	|0|	0	6	0
CaO	0	0	|0|	0	0	0	6
Na_2O	|0|	0	0	0	0	0	6
K_2O	0	0	0	|0|	0	0	6
P_2O_5	0	0	0	0	|0|	1	5

Model results for M12-H subsamples using MC mixing components

samp\mix com	MC	QTZ	MCL	ILM	sum
M12-H1	21.5	76.3	2.1	0.1	100.0
M12-H2	20.9	76.5	2.7	0.0	100.1
M12-H3	18.5	77.7	3.7	0.2	100.1
M12-H4	14.2	77.7	7.9	0.2	100.0
M12-H5	15.4	76.1	8.5	0.2	100.2
M12-H6	16.4	79.2	4.2	0.1	99.9

	<1%	1-2%	2-5%	5-10%	10-20%	20-50%	>50%
MC	2	3	1	0	0	0	0
QTZ	5	1	0	0	0	0	0
MCL	0	0	4	1	0	0	0
ILM	0	0	0	0	1	3	2
SUM	6	0	0	0	0	0	0
SiO_2	|6|	0	0	0	0	0	0
TiO_2	4	0	|2|	0	0	0	0
Al_2O_3	|6|	0	0	0	0	0	0
Fe_2O_3	|6|	0	0	0	0	0	0
MnO	0	1	|1|	2	1	1	0
MgO	1	0	3	|2|	0	0	0
CaO	0	0	|2|	1	2	1	0
Na_2O	|0|	4	1	1	0	0	0
K_2O	0	0	1	|0|	3	2	0
P_2O_5	0	0	1	0	2	|2|	1

| | Vertical lines represent average analytical uncertainty.

low-grade rocks, which we interpret to be those of the sedimentary protolith.

There was selective, macroscopic separation and mobilization of SiO_2 (and perhaps other elements) during metamorphism in the Littleton and Carrabassett Formations. Quartz veins, gneissic banding, and large porphyroblasts are observed in the field in some outcrops. Nevertheless, we have not found evidence of *systematic, long-range,* net gain or loss of SiO_2.

Causes of Compositional Variations in Visually Homogeneous Slate

There is at least a qualitative correlation between composition and proportion of quartz in samples such as the M12-F series (fig. 3A) which have relict graded beds. As other low-grade samples show the same overall compositional characteristics as are seen in the M12-F subsamples, we concluded above that the low-grade samples retain at least some compositional features of the sedimentary protolith. We now examine whether most or all of the compositional characteristics for nonvolatile elements can be understood on the basis of mixtures of common sedimentary and diagenetic minerals of reasonable composition.

We begin by modelling the composition of each 10-g subsample of NH14 as a mixture of sedimentary endmember components, using a least-squares mixing calculation (Bryan, Finger, and Chayes, 1969) for major elements. Hon, Hanson, and Bradley (1991) implied that the protolith of the Carrabassett Formation was a mixture of illite, quartz, and chlorite. We find that we need three principal endmember components (clay, quartz, and chlorite-mica) and a minor one (pyrite) to describe the major-element compositions of the 10-g subsamples of NH14-E precisely. We used a single clay component, because the mixing model cannot effectively use two similar components and often gives a negative value for one of them if two are present. Determining the nature of clay components precisely thus exceeds the ability of the mixing model. A combined chlorite-mica component was used for the same reason. The components used and results of our model are listed in table 5 and shown in figure 6. The required component compositions of the clay and chlorite-mica components are mineralogically proper in that they achieve cation-anion charge balance and fall within the compositional range observed for common sedimentary materials. To derive them, we began with ideal compositions of illite and chlorite and modified them until good fits were obtained for the NH14 subsamples. All adjustments to provide better fitting endmembers preserved the essential character of the minerals. No chemical analysis of minerals was done, nor would any apply; the sedimentary (or diagenetic) minerals of the protolith are unlikely still to be present in the slates, at least not in unmodified form. If the element concentrations of metamorphic rocks can be modelled quantitatively in terms of sedimentary or diagenetic components, the result would be consistent with low-grade metamorphism in which element mobility did not occur over distances sufficient to

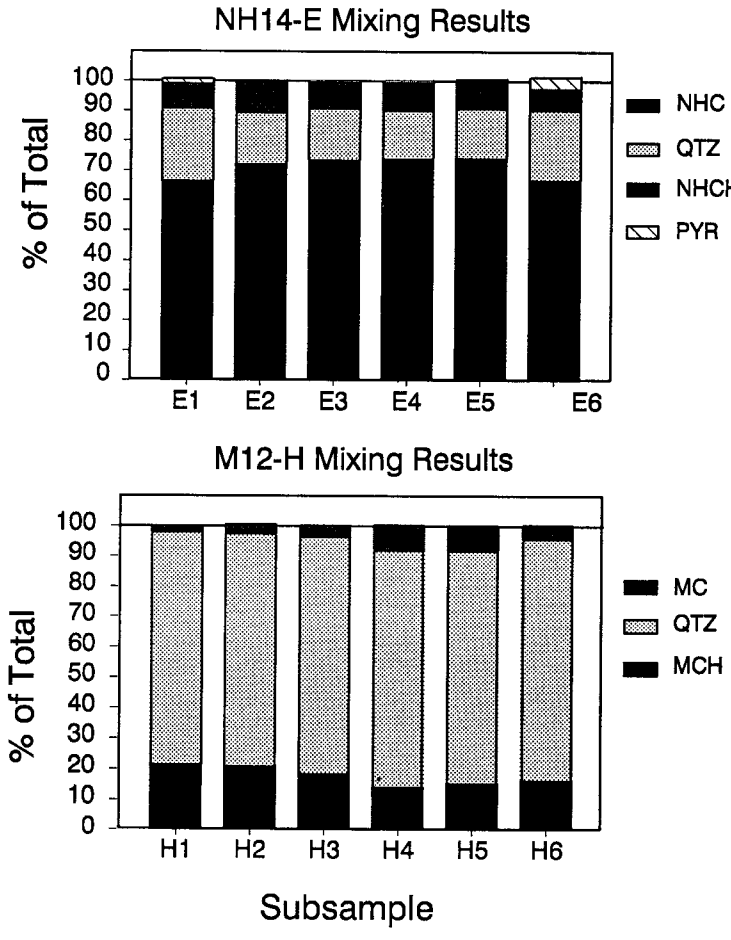

Fig. 6. The stacked bar diagram shows the proportions of each mixing model endmember for individual subsamples of NH14-E and M12-H. Mixing components are defined in table 5 and discussed in the text.

change the bulk compositions of the protolith on the size scale of our subsamples.

The major-element compositions of the individual subsamples of NH14-E can be modeled nearly to within analytical uncertainties as arising from different proportions of sedimentary endmember mixing components of constant composition. These are designated NHC (New Hampshire clay), NHCM (NH chlorite mica), QTZ (pure quartz), and PYR (pyrite); see table 5 and figure 6. All elements were modelled on an LOI-free basis to eliminate effects of devolatization. This tests whether the proportions of non-volatile elements correspond to those of sedimen-

tary minerals, without regard to losses of essential but volatile components of clays, et cetera. Proportions of NHC range from 66.7 to 74.4 percent, of NHCM from 7.3 to 10 percent, of QTZ from 16.1 to 23.9 percent, and PYR from 0.2 to 3.7 percent. These variations are small, yet substantial, considering that they occur within a visually homogeneous block only a few centimeters on a side.

Goodness of fit by the mixing model is determined in several ways. Sums were unconstrained, but in five of six cases (table 5), they were nevertheless within 0.6 of 100 percent, and the worst case was only 101.5 percent. The model uncertainty in the proportion of NHC was always <1 percent and that of QTZ was >1 percent in only one case. Model uncertainties in the minor components NHCM and PYR were higher, but reasonable. Concentrations of total Fe, given as Fe_2O_3 (t), are modeled perfectly, because, lacking the constraint of known S concentrations, the pyrite endmember accounts for any Fe in excess of that corresponding to the best fit for the other elements in Fe-bearing endmembers. Similarly, concentrations of SiO_2 are modeled perfectly, because the QTZ component (table 5) consists entirely of SiO_2. Thus, the uncertainties in model fits for those two oxides have no significance. Except for one TiO_2 value, concentrations of Al_2O_3, TiO_2, and MgO are fit to within ± 1 percent (relative), and their uncertainties are small. Somewhat poorer fits were obtained for the minor constituents MnO, CaO, Na_2O, and P_2O_5. Addition of <1 percent of an apatite component enables better fits for CaO and P_2O_5 within the NH14-E subsamples but adds yet another endmember. (Modelling of trace elements would require still more mixing components, because minor minerals carry significant fractions of them. Detailed modelling of trace elements is beyond the scope of this paper.)

Further discussion is necessary to emphasize the distinction between endmember *components* (that is, the mineral identities of the hypothetical endmembers) and the *chemical compositions* of those components, which we must change slightly as we move from one set of subsamples to another. Although the NH endmember compositions combine to fit the compositions of each NH14-E subsample quite well, they combine to fit the M12-H subsample compositions poorly. We tried altering the NH endmember compositions to provide the best possible fits to the M12-H subsamples consistent with retaining good fits for the NH14-E subsamples but still could not obtain acceptable fits to the M12-H subsamples using the same endmember compositions. Excellent fits to the M12-H subsamples were obtained, however, when the compositions of the clay and chlorite-mica endmembers were changed slightly (MC and MCM, M for Maine, table 5). Specifically, it was necessary to increase the Mg/Fe ratio of the chlorite-mica component and decrease the proportions of exchangeable cations Na and Ca and increase that of K in the clay component to obtain acceptable fits for M12-H subsamples. As M12-H contains no visible pyrite, we omitted the PYR endmember from the calculations; inclusion of a small proportion of endmember ilmenite

(ILM), however, improves the fits. Also, inclusion of a small proportion of a pure iron oxide component reduces somewhat the discrepancy in Mg/Fe. The model even successfully estimated the composition of M12-H6, which is cut by a small quartz vein, as containing only ~3 percent more QTZ than the average subsample. In both cases (NH14-E and M12-H), when the best set of endmembers for each is used, the elements that fit most poorly are the exchangeable cations Ca, Na, and K. This is the same set of elements whose concentrations differ the most between comparable endmembers NHC and MC, and the difference is reasonably explained if exchangeable cation proportions can differ from one location to another only centimeters apart at the time of sedimentation or as a consequence of diagenesis. These compositional differences are not large enough, however, to cast doubt on a sedimentary or diagenetic origin for the main compositional variations of the samples. In a recent study of shale minerology, Block and Hutcheon (1992) found differences of a similar magnitude for their modeled compositions of illites.

(An alternate set of mixing components tried in the modelling of M12-H included albitic plagioclase, composition An_{20}. To make this endmember work, it was necessary to change the compositions of the chlorite-mica and clay endmembers substantially, relative to those used for NH14.)

Thus, the endmember *components* for both the slate and the quartzite are essentially the same, implying that the major protolith minerals were about the same in both locations. The endmember proportions are different, of course, and the endmember *compositions* that explain the compositional variability of 10-g subsamples from the slate must be adjusted slightly to account for similar variability among 10 g subsamples of the quartzite taken ~200 km away. These small differences in endmember composition are consistent with anticipated levels of compositional variability within the sedimentary protolith. Proportions of clay in the 2-kg samples, as sampled by our randomly chosen 10-g subsamples, range from 71 (the average value for NH14-E) to 18 percent (the average for M12-H) and proportions of quartz range from 19 (NH14-E) to 77 percent (M12-H). The subsample-to-subsample variations in mineral proportions as inferred from the mixing model results provide a first-order explanation of the variations in major-element chemical composition among the 10-g subsamples. Although this exercise does not prove that the small scale (10-g subsample) compositional variations are inherited from the protolith, it shows that we can reasonably account for those variations as mixtures of common sedimentary-diagenetic minerals in different proportions. In the case of the quartzites, the compositional differences among the samples correlate with relict sedimentary structure. Thus, we are not compelled to call on low-grade metamorphic processes to produce any of the observed interelement relationships.

Are the compositional variations at the 10-m scale also inherited from the sedimentary protolith? The same endmember components used to model the compositional variations in the 10-g subsamples are

adequate to model the compositions of the 100-g samples, as well. We can almost account for the larger scale heterogeneities indicated by the 100-g samples as more extreme mixtures of the mixing components inferred for the 10-g subsamples. To obtain the best mixing-model fits, however, it is necessary to change the compositions of the endmembers but only slightly and within reason. The required changes are again in the exchangeable elements and the Mg/Fe of the chlorite-mica component. We can thus still understand the compositional differences in terms of reasonable components and reasonable compositional variations among those components in a sedimentary protolith. We cannot, however, use a single set of constant composition endmember compositions to model accurately the major-element compositions even of all the slate samples from the visually homogeneous NH14 outcrop.

The mixing model results have clear relevance to the common practice of normalizing element concentrations to that of a presumably immobile element such as Al_2O_3 or TiO_2 (Ferry, 1982; Ague, 1991; Moss and others, 1995). Given that the composition of a sedimentary protolith may not be constant and that compositional variations can be caused by different proportions of at least three principal minerals, two of which carry significant quantities of Al_2O_3 (and other major elements), there is no reason to expect a single value for an element/Al_2O_3 concentration ratio for individual samples of the sedimentary protolith. Again, we must rely on average values. Thus, in cases where Al and various other elements are immobile during metamorphism, element/Al_2O_3 concentration ratios for those other immobile elements need not be constant among samples of metamorphic rocks or yield the same average as found for sediment samples. A good example here is that of K_2O. Potassium is a significant element only in the clay component, whereas Al is significant in both clay and chlorite-mica. Figure 2C and D show the variations in major element/Al_2O_3 concentration ratios for the NH14-E and M12-H subsamples. In the present case, alumina-normalized ratios show roughly the same amount of spread as the element concentrations themselves (fig. 2A and B), except for SiO_2, for which the spread in the ratio is greater owing to the greater variability of Al_2O_3 concentrations than SiO_2 concentrations in the rocks.

Comparison of Compositional Trends between Low-grade and Higher-grade Rocks; examples of Metamorphic Trends

The variations in major-element concentrations in the low-grade rocks are all consistent with their origin in the sedimentary protolith. The heterogeneity of that protolith at all distance scales studied causes relatively large uncertainties in the average of the element concentrations of low-grade samples, as determined by analysis of tens of samples (first analyzed by Shaw, 1954, and recently by Moss and others, 1995). It also means that sampling is predetermined to be unrepresentative, and that it would be difficult to prove that the rocks of different metamorphic grades developed from the same average protolith. We have shown

above, to the extent that we have data for them, that data for bulk samples of higher-grade rocks lie along the same trends of compositional variation as data for the low-grade rocks (taken to represent the protolith). To find different trends that unambiguously indicate element mobility requires sampling at a smaller distance scale than that of the ~2 kg Shaw samples.

In order to gain some preliminary insight into chemical trends that are clearly a result of metamorphism, we analyzed two 100-g subsamples and six ~10 g subsamples, selected more or less at random, from a massive hand specimen of Littleton quartz-muscovite-staurolite schist (outcrop NH3). Figure 7A compares Al_2O_3 and K_2O data for those samples with data for our 100-g and 10-g low-grade samples. The low-grade subsamples define a fairly tight trend of positive correlation ($r = 0.97$). The staurolite-rich and staurolite-poor subsamples show a strikingly different trend, one that lies at a steep angle to the low-grade sample data, but whose average value plots close to the line. The metamorphic trend is caused by concentration of Al_2O_3 within the staurolite-rich portions of the rock during metamorphism and exclusion of K_2O from them.

We anticipate that a different staurolite-rich rock, one that derived from a portion of the protolith with a lower average Al_2O_3 concentration, would show a similar metamorphic trend, parallel to that of figure 7A but crossing the sediment line farther to the left. We would expect a series of rocks with different initial Al_2O_3 concentrations to produce a scatter of points about the sediment trend that exceeded the scatter observed for low-grade samples. We would also expect the amount of scatter about the sediment trend to decrease with increasing sample mass, as we reach a sample mass over which metamorphism is approximately isochemical.

If extensive scatter were observed for higher-grade samples as large as 2 kg, but not for low-grade samples of that mass, we could conclude that migration had occurred over a distance of at least 7 cm or greater. Figure 7B shows the trend defined by the low-grade samples, the data for the NH3 samples, and the data for the 2-kg low-grade and higher-grade Shaw samples (Moss and others, 1995). The higher-grade data do indeed show more scatter than the 10 and 100-g low-grade sample data, as we would expect for metamorphic gain and loss. The 2-kg Shaw low-grade samples, however, also show more scatter than the 10- and 100-g samples, casting suspicion on an interpretation of metamorphic mobility as the cause of the increased scatter for the equally large medium- and high-grade samples.

Figure 8A, analogous to figure 7A, shows data for Zn and Al_2O_3. Zinc was selected for illustration because of the well-known tendency of staurolite to concentrate that element. As figure 8A shows, a metamorphic trend for Zn also crosses the sedimentary trend at a steep angle. Figure 8B shows that the extent of variation for Zn in the Shaw higher-grade rocks (Moss and others, 1995) does not reach that observed for the 10-g samples of NH3. This suggests that the metamorphic rearrange-

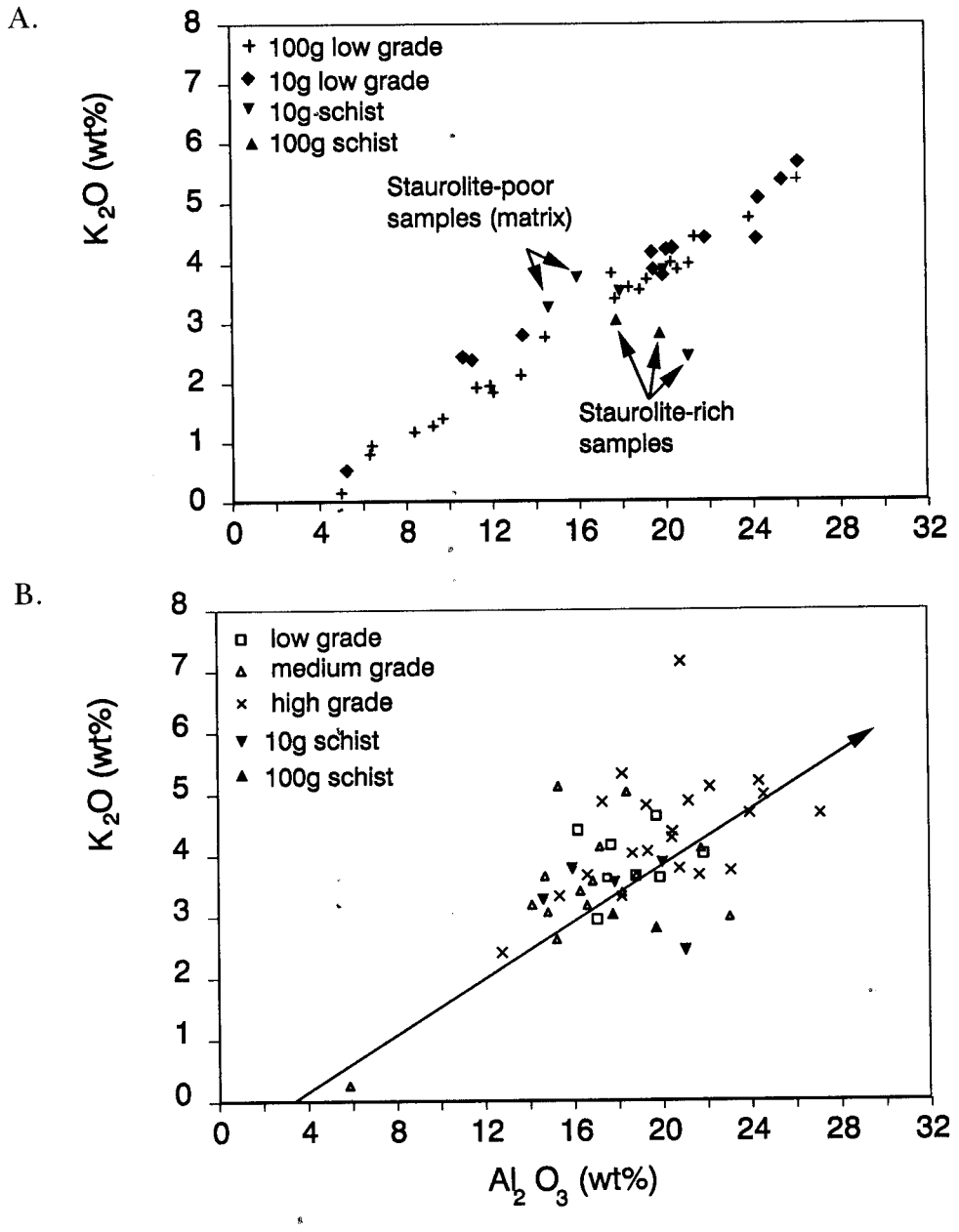

Fig. 7(A) Low-grade Littleton-Carrabassett 10 g and 100 g subsamples show a positive correlation between K_2O and Al_2O_3. Staurolite-rich and -poor samples from a massive staurolite-quartz-muscovite schist fall off the correlation line because staurolite growth has caused a separation of K from Al. (B) The 2-kg hand specimens analyzed by Moss and others (1995) are shown on a diagram similar to A; an arrow represents the trend in A. Values for the staurolite schist are included. The scatter for higher-grade samples (upright triangles and Xs) scarcely exceeds that for lower-grade 2 kg samples (squares).

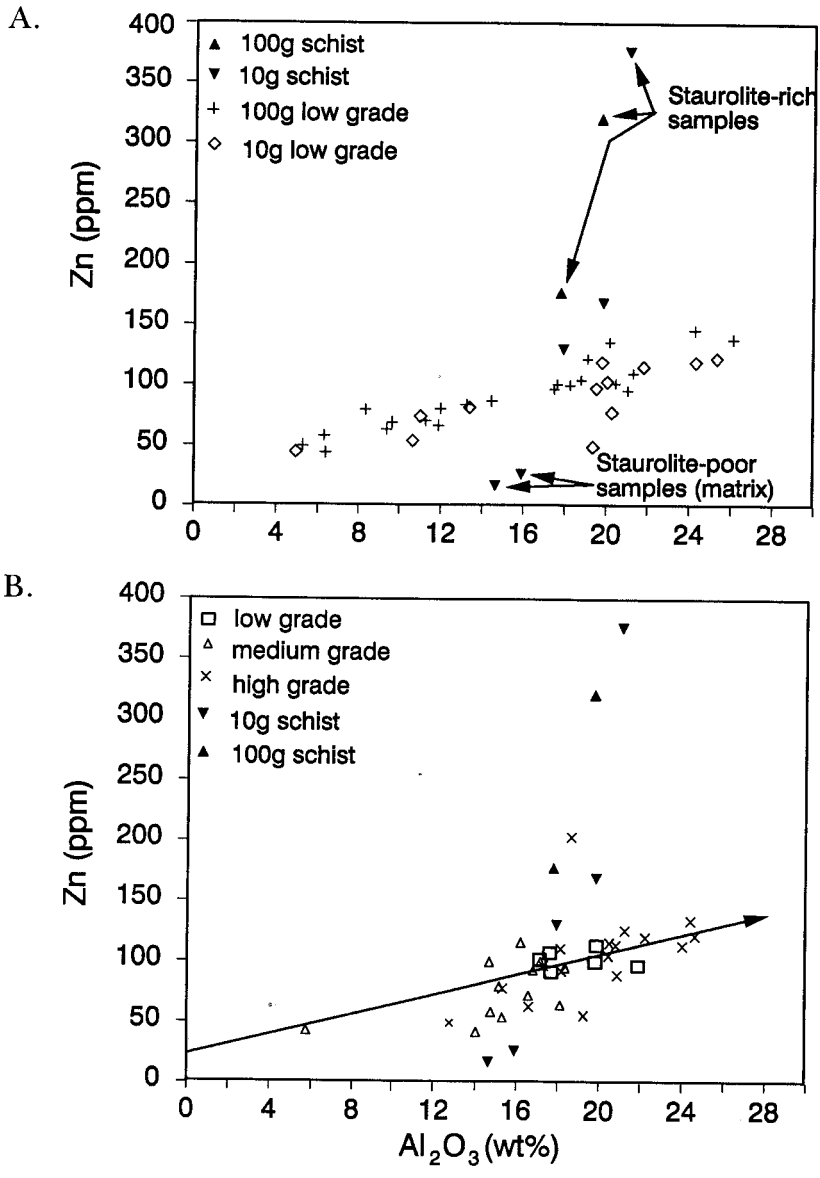

Fig. 8(A) Low-grade Littleton-Carrabassett 10 g and 100 g subsamples show a positive correlation between Zn and Al_2O_3. Both low-grade subsamples and staurolite schist subsamples show positive correlations for Al_2O_3 and Zn, but the correlation is steeper for the metamorphic samples because Zn is more strongly concentrated in staurolite than Al is. (B) The 2-kg hand specimens analyzed by Moss and others (1995) are shown on a diagram similar to A; an arrow represents the trend in A. Values for the staurolite schist are included. The scatter for higher-grade samples (upright triangles and Xs) scarcely exceeds that for lower-grade 2 kg samples (squares).

ment of Zn observed at the 10 g scale is not readily observed at the 100 g scale. Presumably, the scale of movement of Zn matches that of the major elements that produced the staurolite in the schist (NH3), which was already evident on inspection of the hand specimen, which contained centimeter-sized staurolite crystals. Trace-element migration over similar or greater distances might occur during conversion of sediment to metamorphic rocks lacking large porphyroblasts, and there the scale of migration would be less obvious. The observation of significant compositional deviation from the sediment trend would show that such migration had occurred.

CONCLUSIONS

The following conclusions are based on our study of mainly major-element compositional variations of low-grade metamorphic Littleton-Carrabassett rocks at distance scales of centimeters, tens of meters, and several kilometers, plus comparison with previously analyzed rocks of higher grade:

1. Even the most visually homogeneous Littleton-Carrabassett slate is compositionally variable within a single 2-kg hand sample on a 10-g subsample scale. Also, the variability among 100-g samples taken 10 m apart in a visually homogeneous slate outcrop exceeds that of the 10-g subsamples from a single hand sample. Compositions of 10-g subsamples from a visually homogeneous 2-kg quartzite sample are more variable than those from the slates. Compositions of samples from different locations in quartzite outcrops are more variable still, consistent with the presence of relict turbidite bedding. Compositions of single 100-g samples from seven different outcrops show even more compositional variability than the range found for the 10-g quartzite subsamples selected to represent probable compositional extremes.

2. The compositional variations in the low-grade metamorphic rocks can be explained quantitatively in terms of reasonable variations in proportions of clay, quartz, chlorite-mica components in the sedimentary protolith. The compositions of the clay and chlorite-mica components must be adjusted, within reason, to match the compositions of the samples if the samples were taken more than a few centimeters apart. Such adjustments are for Na, K, and Ca concentrations in the clay and for the Mg/Fe in the chlorite-mica.

3. Higher-grade Littleton samples follow the same compositional trends as the low-grade samples. In both, the SiO_2-Zr trend is a positive one, characteristic of a sedimentary quartz-zircon association, rather than metamorphic mobilization. Among ~10-g subsamples of staurolite schist, metamorphic trends were observed consistent with a short transport distance of the order of a few centimeters at most.

4. Because the medium- and high-grade metamorphic rocks of the Littleton and Carrabassett Formations retain the pattern of compositional variations characteristic of the sedimentary protolith over the entire range of sample masses and collection distances, compositional

data from such metamorphic rocks can provide information on the nature of the sedimentary protolith.

5. The compositional variation among the Littleton-Carrabassett rocks is apparently inherited from a sedimentary protolith that had at least two Al_2O_3-bearing, major mineralogical components (clays and chlorite-mica). The ratios of individual elements to Al_2O_3 in the protolith are thus not constant, so element concentrations normalized to Al_2O_3 (or perhaps to other immobile elements) in metamorphic rocks need not be a sensitive indicator of mobility of those elements.

6. The protolith was heterogeneous to about the same extent on all distance scales. Relict turbiditic bedding was evident in some low-grade outcrops, and some low-grade, homogeneous outcrops derived from more quartz-rich protolith than others. The nature of the protolith can be visually obscure in higher-grade rocks. Thus, for purposes of comparing average compositions, it is risky to exclude rocks with extreme compositions from either the population of sedimentary or low-grade metamorphic rocks or the population of higher-grade metamorphic rocks on the basis that they are the wrong type or that they derived from a protolith of the wrong type. For example, if one investigates compositional variations in pelites, and quartz-rich samples are eliminated from the population of low-grade rocks because they (obviously) derived from quartz-rich protolith, metamorphic rocks deriving from similar protolith may not be recognized as such, and their high SiO_2 concentrations may be erroneously attributed to silica mobilization during metamorphism.

7. If samples have different compositions because they contain different proportions of sedimentary components, there is no a priori reason that concentrations for any element, trace or major, would be normally or lognormally distributed. Mineral proportions are subject to closure; they cannot vary randomly. Even if mineral compositions are fixed, or if they vary normally, linear combinations of minerals will not necessarily produce a normal or a lognormal distribution of concentrations. If an element is carried almost exclusively by a minor or trace mineral, its carrier need not be randomly distributed within a sediment, because non-random processes such as sorting may influence the proportion of that mineral in a given sample. Even if proportions of individual carriers did vary normally, if there is more than one significant carrier for an element, its concentrations in the mixture need not vary normally because random linear combinations of carriers with different average concentrations of an element are not constrained to yield normally distributed concentrations. Thus, for understanding compositional variations, models that take into account causes of compositional variation (such as mixing models) are likely to yield more insight than statistical analysis of concentration variations alone. Mixing models are also no panacea; they readily show what mixtures of chosen components cannot explain compositions, but the value of a good fit is no better than the accuracy of selection of endmembers and their compositions. Such models readily indicate mixtures that are incorrect, however.

8. If differences among *average* compositions of rocks of different metamorphic grades are the principal means of determining whether there has been large-scale gain or loss of an element, then representative sampling is crucial but may be virtually impossible in practice. In the case of the Littleton-Carrabassett rocks, because their compositions cover a large range, we cannot expect to obtain a compositional average with a small standard deviation. It would also be difficult to demonstrate that any sample suite was compositionally representative of its metamorphic grade throughout the entire outcrop area of the formation, or that sets of rocks of different metamorphic grade all derived from portions of the protolith that had the same distribution of compositional and physical characteristics.

9. Apparent retention of protolith interelement character in 2-kg samples of highly metamorphosed rock bodes well for use of detailed compositional data on metamorphic rocks to study the nature of their sedimentary protolith on intermediate and large distance scales.

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