CHROMIUM AND NICKEL IN SHALE OF THE TACONIC FORELAND: A CASE STUDY FOR THE PROVENANCE OF FINE-GRAINED SEDIMENTS WITH AN ULTRAMAFIC SOURCE

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ABSTRACT: **To test the suitability of using shale geochemistry as a provenance indicator of a source with an ultramafic component, we used I.C.P. Mass Spectrometry to analyze 130 samples from seven localities from Newfoundland to New York. These samples represent mud from the foreland basin produced during the collision of the Taconic arc with North America in the Ordovician. The sandstones in the flysch contain detrital chromite and other detritus that indicate that the source contained ultramafic rocks, presumably from ophiolites emplaced during collision. This setting is an ideal test case for examining the spatial and temporal variation in Cr and Ni geochemistry of shale derived from ophiolite-bearing highlands. Shale samples with high concentrations of Cr and Ni have a Cr/Ni ratio of ~ 1.4, which is approximately the Cr/Ni ratio for ultramafic rocks (~ 1.6), suggesting only minor geochemical partitioning, but sandstones have a Cr/Ni ratio of > 3.0, suggesting significant sedimentary fractionation. Analyses of samples taken upsection in a single stratigraphic section suggest that proximity to the source influences Cr and Ni concentrations. A decrease in Cr and Ni concentrations through time suggests that uplift and erosion of the thrust complex (non-ophiolitic) diluted the ultramafic signal. We attribute significant along-strike variation in Cr and Ni concentrations to the relative proportion of ultramafic rocks in the source region. This case study shows that Cr and Ni geochemistry of shale from basin strata can be used to determine the lateral and temporal variability of ultramafic rocks in an active orogenic setting.**

INTRODUCTION

In ancient collisional settings the timing, duration, and spatial variation in tectonic activity are assessed mainly by analysis of the preserved sedimentary record in adjacent foreland basins. Ophiolites, which are widely thought to represent slabs of upper mantle and oceanic crust, commonly have a significant component of ultramafic rocks that are geochemically distinct from other rocks at the surface of the earth (see Coleman 1977; Moores 1982; Hamilton 1988). In many collision zones, ophiolites mark the suture between different lithotectonic assemblages, especially in island-arc collisions. Although several techniques have been used to determine the presence of ultramafic material in sedimentary detritus, our goal here is to explore the benefits of using shale geochemistry as a provenance indicator of ultramafic rocks, because the timing of their uplift is commonly important in tectonic reconstructions.

The complexity of collision zones underscores the importance of analyzing both lateral and vertical trends in the sedimentary record in ancient sequences. For example, modern collision of the Luzon arc against the passive margin of Asia is diachronous in that collision is progressing from north to south (Lundberg and Dorsey 1988; Lundberg 1994). The collision of the Indonesian arc with the passive margin of Australia is similarly diachronous in that collision is well advanced directly to the north of Australia, where deformed rocks have been uplifted in New Guinea, but incipient to the northwest near Timor (e.g., Hamilton 1979; McCaffrey et al. 1985).

Understanding the timing of emergence of ultramafic rocks in collision zones is not the only motivation for examining Cr and Ni geochemistry of shale. Detailed studies of stratigraphic sections deposited adjacent to volcanic arcs have been used to determine the timing, duration, and extent of uplift of ultramafic-bearing rock in: (1) outer-arc ridges to forearc basins, such as in Lower Cretaceous rocks of the Great Valley Sequence in California (Suchecki 1984) and modern basins in Sumatra (Beaudry and Moore 1985) or Luzon (Bachman et al. 1983); or (2) backarc basins (Nichols et al. 1991). In synorogenic settings other than the Taconic foreland, heavy-mineral suites, including chromite, have been used to link source regions to flysch sequences deposited in nappe complexes (Garver 1992; Winkler and Slaczka 1992), and stratigraphic analysis of sediments deposited on ophiolites can resolve the timing of emplacement (Schweller et al. 1984).

This paper presents new geochemical data from shale deposited in the foreland basin from Newfoundland to New York in both older (allochthonous) sequences and younger (autochthonous) sequences to demonstrate the lateral and temporal variation of Cr and Ni in the synorogenic strata. Our goal is to show that Cr and Ni in shale is a sensitive indicator of ultramafic provenance but that their concentrations are probably affected by the volume of ultramafic rocks in the source area and by dilution from Cr- and Ni-poor rocks. We suggest that in many of the cases discussed above, shale geochemistry can provide insight into determining the timing and extent of ultramafic-derived detritus.

PROVENANCE INDICATORS OF ULTRAMAFIC ROCKS

Ophiolites are composed of pillow basalts and pelagic sediment underlain by gabbros and ultramafic rocks, which are collectively thought to represent part of the oceanic crust and upper mantle (Coleman 1977; Moores 1982). In terms of the geochemistry of sediment shed from ophiolites, the ultramafic rocks are by far the most distinctive lithology. Geochemically, the ultramafic rocks, which may constitute only a small percentage of an ophiolite, are distinctive because the concentrations of Cr and Ni are orders of magnitude greater than all other rocks commonly exposed at the surface (Goles 1967; Coleman 1977).

Most provenance studies involving ultramafic rocks in a source area examine sandstones for either heavy-mineral suites or geochemistry; only a few have used shale geochemistry. Detrital chromite in sandstones has been interpreted to signify the existence of ultramafic rocks in source regions, because few other rocks contain chromite (Björlykke 1974; Hiscott 1984; Garver 1992). Although detrital chromite probably indicates a partial ultramafic source, problems arise if sandstone composition is relied on for provenance evaluation, because mineral dissolution may be significant due to high permeability (e.g., Hiscott 1985; Shanmugam 1985). Most minerals in ultramafic rocks, such as olivine, pyroxene, and serpentine, are chemically and mechanically unstable, so the bulk of the detritus derived from ultramafic rocks will probably be found in the fine fraction of sediments derived from a terrane composed partly of ultramafic rocks.

Surprisingly, few studies have used shale to investigate the abundance and distribution of ultramafic rocks in a source region. Much of the work that has been done has focused on Archean rocks (e.g., Danchin 1967; McLennan et al. 1983; Wronkiewicz and Condie 1987), when the composition of the crust and surface processes were much different than in the Phanerozoic. Several studies have used Cr and Ni concentrations in Phanerozoic shale as a provenance indicator for ultramafic rocks (e.g., Papavassiliou and Cosgrove 1982; Yucesoy and Ergin 1992; Thiébault and Clément 1992; Garver and Royce 1993; Garver and Scott 1995). The high correlation between Cr and Ni in clay-size detritus, Cr/Ni ratios between

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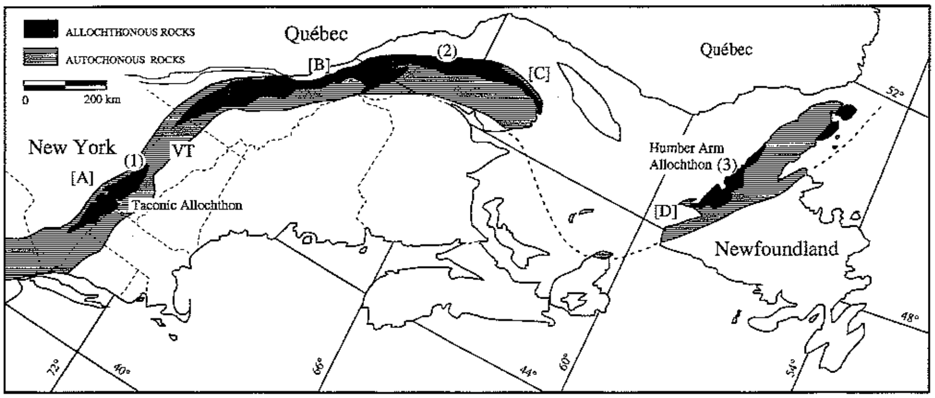

FIG. 1.—Map showing the regional setting and location of individual study areas. Shaded areas are miogeoclinal rocks of the former margin of eastern North America that were deformed during the Taconic orogeny. Black areas are allochthons that were displaced during the Taconic orogeny. Approximate sample locations include (autochthonous sequences designated with letters, allochthonous sequences designated with numbers): [A] Schenectady/Albany New York; (1) Pawlet, Vermont; [B] Québec City, Québec; (2) Tourelle, Québec; [C] Cloridorme, Québec; [D] Port au Port Peninsula, Newfoundland; and (3) Cow Head, Newfoundland. Modified from Williams and Cawood (1989).

1.4 and 1.6, and the presence of ultramafic rocks in the source region in all of these studies suggest a nearly complete and unfractionated transfer of Cr and Ni from the source.

TACONIC OROGENY

We chose to study sediments of the Taconic foreland basin, because the stratigraphy and tectonic setting are well established and previous studies have documented that the source contained ophiolites. Ordovician tectonism along eastern North America was dominated by the collision of the west-facing Taconic arc with the passive margin of North America in the Middle to Late Ordovician. Near the surface, the collision was characterized by denudation of ophiolites and imbricate thrusting within an advancing orogenic wedge and deposition in an adjacent foredeep (Church and Stevens 1971; Williams 1975; Nelson and Casey 1979; Hiscott 1978; Rowley and Kidd 1981; Shanmugam and Lash 1982; Stanley and Ratcliffe 1985; Pickering et al. 1988; Bradley and Kidd 1991). The progressive emplacement of the Taconic arc onto the edge of the continent resulted in nearly continuous deposition of flysch in an adjacent foreland basin in which the locus of deposition migrated progressively toward the continent (Pickering 1987). This forward progression resulted in older flysch that is allochthonous and was involved in the advancing thrust complex, and younger flysch that is autochthonous and only mildly deformed. Bear in mind that the allochthonous flysch records the early phase of collision whereas the autochthonous flysch records the erosion of the Taconic highlands during the final phase of collision.

It is well known that ultramafic rocks were in the source area of the Taconic foreland basin. Several studies have shown that flysch of the Taconic orogeny contains detrital chromite and ultramafic detritus derived from the ultramafic component of ophiolites in the source (Hiscott 1978; Nelson and Casey 1979; Rowley and Kidd 1981; Hiscott 1984; Quinn 1988). Sandstones of the flysch locally contain detrital serpentine and chromite that vary in abundance along strike, presumably reflecting changes in the proportion of ultramafic rocks in the source area (Hiscott 1984). The presence of detrital chromite, principally in flysch of Québec and Newfoundland (Enos 1969; Hiscott 1978, 1984; Quinn 1988) but also in Ordovician rocks of the Taconics in Vermont (Rowley and Kidd 1981; B. Baldwin, personal communication, 1990), has been interpreted to signify erosion of ophiolites in the source during collision.

Hiscott (1978) evaluated the provenance of the allochthonous Tourelle Formation, exposed on the Gaspé Peninsula ("D" in Figure 1), which is composed of sandstones rich in quartz, feldspar, and volcanic rock fragments. It is chromite in the accessory minerals, however, that suggests that these sandstones have a partial ultramafic provenance. Hiscott estimated that these sandstones (with ~ 300 ppm Cr) were derived from a source area composed of ~ 7% ultramafites. Later, Hiscott (1984) used XRF to analyze 177 sandstones from synorogenic strata from Tennessee to Newfoundland. By analyzing Cr, Ni, V, Cu, Ti, Zr, and Y, he determined that Cr and Ni are elevated in flysch north of the U.S.-Canada border, and a factor analysis of the data indicated that a single factor controlled Cr and Ni concentrations, which he interpreted to be an "ophiolite factor." Likewise, Rowley and Kidd (1981) recognized that rocks involved in the Taconic orogeny in western New England (Vermont and New York) differed from rocks to the north (Québec and Newfoundland) because, unlike areas to the north, New England lacked a wide ophiolite-floored forearc prior to collision. Therefore, not only does the modern distribution of ophiolites support the suggestion of Rowley and Kidd (1981), but, more importantly, the provenance of sandstones as determined in Hiscott's (1984) study suggests that highland composition changed systematically from north to south. Here we assume the validity of these results and explore the implications for shale geochemistry.

METHODS

We collected and analyzed 135 shale samples: 46 from eastern New York, 6 from western Vermont, 20 from Québec, and 63 from western Newfoundland (Fig. 1, Table 1). The Goose Tickle, Cloridorme, Tourelle, Normanskill, and Schenectady Formations were sampled in several different localities, and the other units were sampled at only one site. To minimize stratigraphic heterogeneity, each 200 g sample was collected over a 10 cm vertical interval.

Samples were washed, dried, and crushed into a fine powder using a silica mortar and pestle. The powdered sample was then weighed and ignited in a box furnace at 950°C for 1 hr. After igniting, part of the ignited sample was weighed and dissolved using HF and HNO_3. Ti, V, Cr, Mn, Co, Ni, and Cu were analyzed, with Sc, Nb, and Ga as internal standards, using a VG Inductively Coupled Plasma Mass Spectrometer in the Geology Department at Union College. National Bureau of Standards Sample 688 was used for concentration calculations (Govindaraju 1989). Machine drift during each of the ten separate runs was corrected using blanks and standards at both the beginning and end of each run sequence. Each sample was run in duplicate, and all data used in this study represent the average of the two duplicates. All concentrations are relative to the anhydrous mass of the rock. The percent error was calculated for the average between all samples; the average relative deviation for the mean values is 3% for Cr and Ni.

RESULTS

From our data, several observations on lateral trends, vertical trends, and grain-size effects are outlined in detail below (Figs. 2–4). Comparison between Cr and Ni in shale (our results) and sandstone samples from the same units (Hiscott 1984), shows two important trends (Fig. 3): (1) high Cr concentrations, presumably related to detrital chromite, are pronounced

TABLE 1.—*Average concentrations of shale from different formations analyzed for this study**

	Ti	V	Cr	Mn	Co	Ni	Cu
			Newfoundland				
Autochthonous							
Rocky Harbour Mélange (n = 5)	**0.72**	**134.9**	**144.5**	**0.06**	**18.7**	**84.3**	**49.6**
SD	0.09	15.0	54.3	0.01	7.02	46.2	8.73
Goose Tickle Fm (n = 26)	**0.76**	**157.0**	**112.7**	**0.08**	**15.8**	**73.0**	**56.5**
SD	0.13	30.9	25.6	0.07	4.92	17.7	12.1
Black Cove Fm (n = 4)	**0.60**	**215.5**	**92.0**	**0.04**	**15.45**	**67.1**	**74.4**
SD	0.06	93.88	8.88	0.00	0.97	6.63	10.1
Table Cove Fm (n = 5)	**0.51**	**145.6**	**88.8**	**0.06**	**17.9**	**53.4**	**47.4**
SD	0.05	96.1	8.28	0.01	3.16	5.52	20.5
Mainland Sandstone (n = 5)	**0.77**	**152.2**	**157.4**	**0.08**	**19.4**	**118.3**	**50.2**
SD	0.03	8.14	22.38	0.01	2.96	31.8	6.80
Cape Cormorant Fm (n = 10)	**0.57**	**111.3**	**93.2**	**0.03**	**17.4**	**58.5**	**51.2**
SD	0.11	14.1	20.3	0.01	1.65	7.11	9.94
Allochthonous							
Cow Head Group (n = 3)	**0.65**	**179.3**	**103.1**	**0.02**	**14.5**	**47.5**	**44.2**
SD	0.17	124.5	24.5	0.00	2.86	11.0	13.5
Lowerhead Fm (n = 5)	**0.99**	**226.6**	**252.3**	**0.07**	**30.7**	**230.5**	**59.7**
SD	0.07	34.8	41.1	0.01	4.55	44.6	9.72
			Quebec				
Autochthonous							
Lotbiniere Fm (n = 2)	**0.62**	**106.0**	**126.0**	**0.07**	**18.2**	**70.0**	**39.0**
SD	0.00	8.00	49.0	0.01	2.60	17.0	2.00
Neuville Fm (n = 1)	**0.72**	**51.0**	**32.0**	**0.04**	**12.2**	**15.0**	**9.00**
SD	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cloridorme Fm (n = 9)	**0.81**	**135.3**	**167.5**	**0.06**	**21.3**	**111.5**	**45.8**
SD	0.09	18.2	36.3	0.01	4.42	46.9	13.7
Allochthonous							
Tourelle Fm (n = 8)	**0.93**	**144.0**	**187.3**	**0.10**	**24.5**	**153.3**	**46.5**
SD	0.09	19.9	27.3	0.11	2.44	33.4	6.72
			Vermont/New York				
Autochthonous							
Normanskill Fm (n = 10)	**0.92**	**132.0**	**91.0**	**0.06**	**35.4**	**53.0**	**53.0**
SD	0.07	8.00	5.00	0.01	12.2	13.3	5.00
Schenectady Fm (n = 20)	**1.15**	**197.0**	**150.0**	**0.07**	**22.9**	**70.0**	**66.0**
SD	0.31	52.0	48.0	0.01	7.40	20.0	17.0
Utica Shale (n = 13)	**0.40**	**60.0**	**49.0**	**0.05**	**16.1**	**44.0**	**32.0**
SD	0.11	25.0	10.0	0.01	3.50	9.00	9.00
Larrabee Fm (n = 3)	**0.36**	**38.0**	**51.0**	**0.05**	**15.4**	**27.0**	**15.0**
SD	0.09	3.00	14.0	0.02	4.60	7.00	9.00
Allochthonous							
Pawlet Fm (n = 6)	**0.95**	**144.4**	**89.1**	**0.06**	**15.8**	**47.3**	**57.8**
SD	0.28	41.6	16.9	0.03	4.21	8.50	20.3

* Each sample value represents the average of duplicate runs and all samples for individual formations have been averaged for this table. The values of all elements are given in parts per million except titanium and manganese (which are in weight %). The individual sample data are available from the authors. The average relative error for each element is as follows: Ti (2.5%); V (2.4%); Cr (3.1%); Mn (3.5%); Co (2.9%); Ni (2.9%); and Cu (3.6%). SD is the standard deviation.

in the sandstones, but the correlation between Cr and Ni is weak; (2) Cr and Ni concentrations in shale have a strong positive correlation ($r \geq 0.90$).

In an attempt to identify the site of the Cr and the Ni in the shale, we determined the mineral content and trace-element concentrations of > 2 μm and < 2 μm size fractions of a single shale sample (Lowerhead Formation; see Table 1) with 261 ppm Cr and 217 ppm Ni using X-ray diffraction and then I.C.P. mass spectrometry. The XRD patterns of this sample indicate that the dominant mineralogy in the < 2 μm fraction is illite and chlorite plus some quartz and feldspar; no serpentine peak was detected, which was not the case in another study where high concentrations of Cr and Ni were identified in shale (Thiébault and Clément 1992). The > 2 μm fraction contains mostly quartz and feldspar, plus some illite, chlorite, and minor pyroxene (diopside). The < 2 μm size fraction contains ~ 318 ppm Cr and 293 ppm Ni, whereas the > 2 μm fraction contains 108 ppm Cr and 43 ppm Ni. These data suggest that the bulk of the Cr and Ni is in the clay size fraction.

To study proximity of the source region and the effects of depocenter migration, we analyzed upsection changes in shale geochemistry in two autochthonous stratigraphic sections: one from New York, where few ultramafic rocks seem to have been present in the source, and one from Newfoundland, where a substantial part of the source is inferred to have been ultramafic. In general, Cr and Ni increase upsection in the two stratigraphic sections, as best shown in the autochthonous section in Newfoundland ("D" in Fig. 1; Fig. 2A). The base of the section has Cr and Ni values of < 100 ppm and show a clear increase upsection. There is a sharp increase in Cr and Ni in the flysch of the Mainland Sandstone, which has detrital chromite (Quinn 1988). Below the Mainland Sandstone, however, there is a slight increase in Cr and Ni, and at this stratigraphic position Cr/Ni ≈ 1.4, and this ratio is maintained upsection.

Cr and Ni concentrations increase upsection also in the Schenectady Formation and underlying Utica Shale of the Mohawk Valley in New York ("A" in Fig. 1; Fig. 2B), but Cr/Ni is relatively high in the Schenectady Formation and the concentrations are rather erratic. In the Schenectady Formation, Cr/Ni ≈ 2.1, much higher than correlative sequences to the north.

Although the vertical sections give an idea of changes in basin geometry with respect to the source region over a rather short time interval, longer temporal changes in the source region can be seen by a comparison of young autochthonous flysch deposits to older and deformed allochthonous sequences (Fig. 4). In sequences with relatively high concentrations of Cr and Ni (i.e., Québec and Newfoundland), the older allochthonous sequences contain more Cr and Ni than the younger autochthonous sequences. Compare, for example, Cr and Ni values for the Mainland Sandstone and Goose Tickle Formation (autochthonous) and the Lower Head Formation (allochthonous) of Newfoundland, or the Cloridorme Formation (autochthonous) and the Tourelle Formation (allochthonous) of Québec (Fig. 4; Table 1).

Average Cr and Ni values systematically decrease from north to south along the orogen (Fig. 4). The highest Cr and Ni concentrations were found in shale samples from allochthonous and autochthonous sequences in Newfoundland and less so in Québec; samples from New York and Vermont are even lower. This trend is well pronounced in the allochthonous sequences (Fig. 4).

DISCUSSION

Elevated concentrations of Cr and Ni in shale and sandstone (Fig. 3) are interpreted to indicate ultramafic rocks in the source region. Higher concentrations of Cr in sandstone presumably reflect fractionation in the sedimentary cycle, by which chromite is preferentially concentrated. In shale, the variation of Cr and Ni is more uniform than in sandstone from identical units, and the variation within shale spans a relatively narrow range (Fig. 3). Background values of Cr and Ni in shale are fairly well estimated by the North American Shale Composite (N.A.S.C.) values, which are 105 ppm Cr and 60 ppm Ni (Fig. 3; Gromet et al. 1984). Unfortunately, some of the samples that constitute the N.A.S.C. are from the same Cr- and Ni-rich shales discussed in this paper; this may mean that the N.A.S.C. values for these elements are too high.

Trends in the Taconic Foredeep

Assuming that shales with relatively high Cr and Ni concentrations had a partly ultramafic source, our data confirm the findings of other workers that the Taconic foreland had an ultramafic source that varied along strike and through time. A detailed analysis of an individual stratigraphic section can provide useful information about the first appearance of a significant proportion of ultramafic rocks in the source region. For example, note that in the stratigraphic section from Newfoundland (Fig. 2), Cr/Ni ≈ 1.4 in shale of the Cape Cormorant Formation, well below the chromite-bearing clastics of the overlying Mainland Sandstone. In this case, we suggest that it is lower part of the Cape Comorant Formation (Cr/Ni ≈ 1.4) that provides the first strong evidence of unroofing of ultramafic rocks in the highlands; the chromite-bearing sandstones in the overlying flysch simply represent the continued erosion of this source.

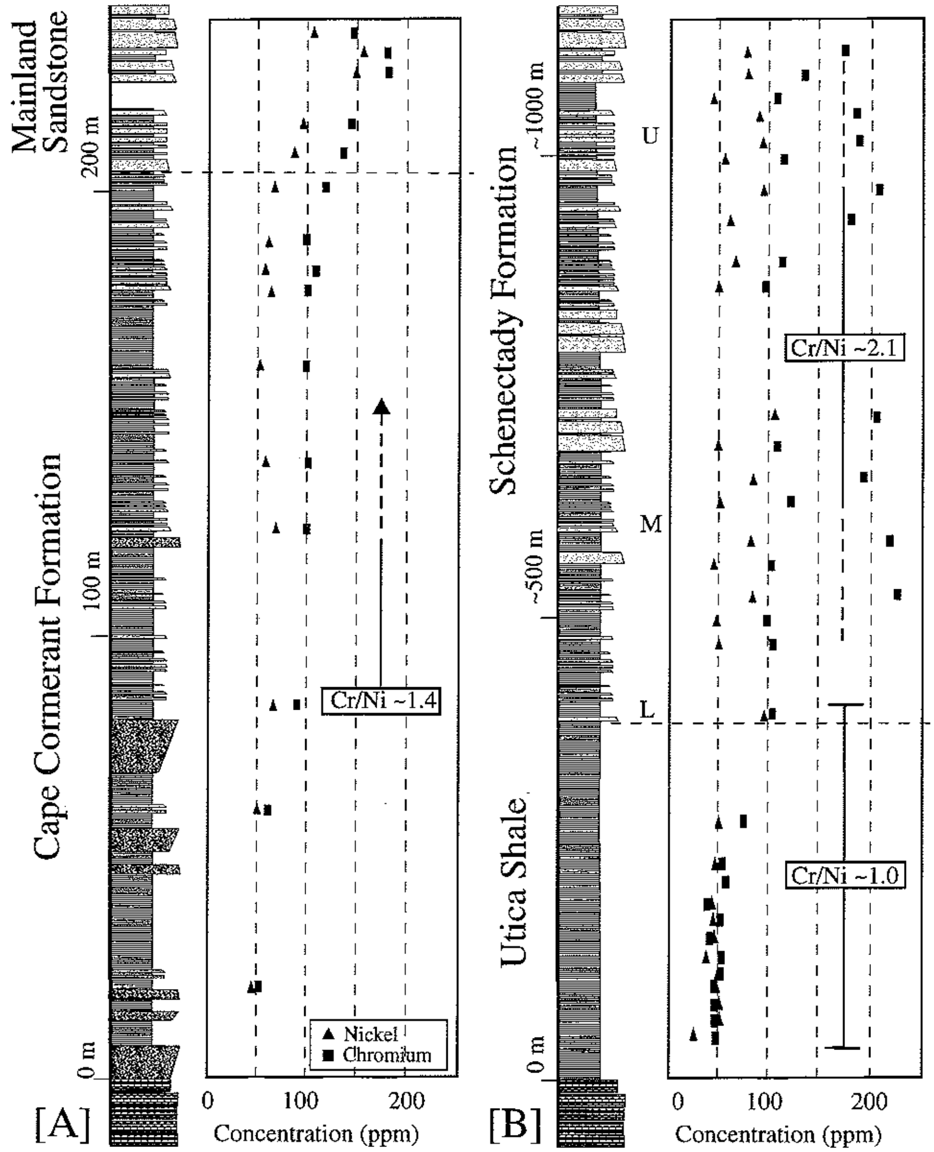

FIG. 2.—Generalized stratigraphic sections showing the variation in Cr and Ni upsection in autochthonous foreland deposits to the Taconic orogeny. Shown here are the only complete stratigraphic sections that were systematically sampled. **A)** Generalized stratigraphic section of the synorogenic units on the Port-Au-Port Peninsula, Newfoundland. **B)** Composite and generalized stratigraphic section of the Schenectady Formation in the Mohawk Valley of eastern New York.

One important characteristic of our data set is that the Cr and Ni concentrations are higher in the older allochthonous rocks and lower in the younger autochthonous rocks that record the final stages of tectonism (Fig. 4). In general, the allochthonous flysch sequences are upper Arenigian to lower Caradocian (upper Lower to lower Upper Ordovician), whereas the autochthonous flysch is upper Llanvirnian to Ashgillian (Middle to Upper Ordovician; see discussion in Hiscott 1984). We entertain two different interpretations for the differences in Cr and Ni concentrations between younger and older foreland-basin strata. (1) The decrease in Cr and Ni though time could have resulted from erosional removal of ultramafic rocks from the source. This scenario seems unlikely because ophiolites are still present today, although they may have been structurally buried at the time. (2) If the proportion of ultramafic rock remained more or less constant, incorporation and uplift of sedimentary rocks into the thrust wedge in front of the colliding arc could have resulted in dilution of the ultramafic signal through time (Fig. 5). Through time the leading edge of deformation front rides up onto the North American margin and older passive-margin sequences and allochthonous basin strata are uplifted, eroded, and redeposited into the foreland basin (''autochthonous flysch'' in Figure 5B). Presumably, the ophiolitic signature in the sedimentary record is diluted by the addition of these sedimentary rocks. Therefore, through time at any one locality, a decrease in Cr and Ni concentrations should be expected if the thrust complex associated with the ultramafic rocks becomes emergent. A scenario similar to this second possibility was envisioned by Rowley and Kidd (1981) to explain the evolution of the Taconic orogeny in New England (Fig. 5). In other collisional settings, the stratigraphic level where Cr and Ni concentrations decrease may correspond to erosion of the thrust complex after uplift above sea level.

Trends along strike suggest that a lower proportion of ultramafic rocks were in the source region for the sediments in New York and Vermont. For example, in the Mohawk Valley of eastern New York, Cr concentrations in the autochthonous Schenectady are higher than in the partly correlative but slightly older Normanskill Formation (Fig. 4), but Ni concentrations are not. In the Schenectady Formation, Cr/Ni ≈ 2.1, and Cr correlates well with vanadium and titanium, both of which are elevated (Table 1). We interpret these elevated Cr values to reflect, in large part, a significant mafic volcanic component in the source region. Because the Cr was presumably derived from a source dominated by mafic volcanic rocks, the

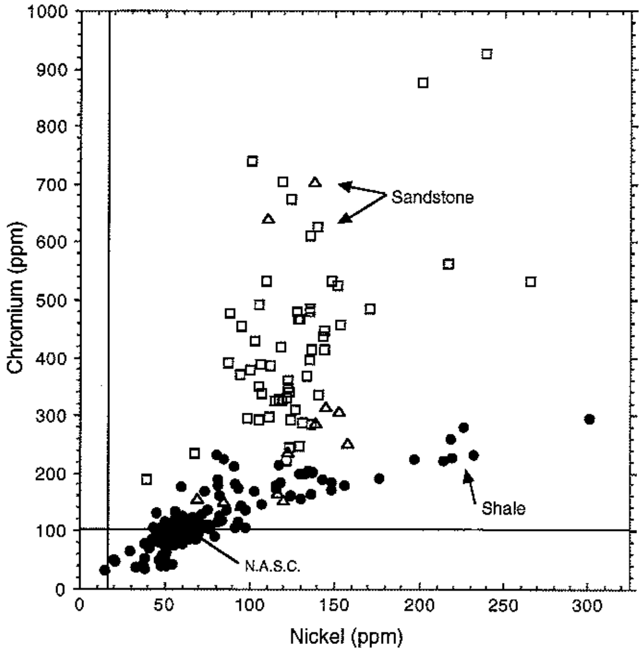

FIG. 3.—Chromium vs. nickel for all shale (solid circles) and sandstone (open triangles) samples (Royce, unpublished). Sandstone analyses of Hiscott (1984) are also shown (open squares). Although Hiscott's study included many other units, this graph includes only those formations considered in this study. The North American Shale Composite (N.A.S.C.; vertical and horizontal lines) has average values of chromium (105 ppm) and nickel (60 ppm).

Cr/Ni ratio is greater than if the Cr had been derived from ultramafic rocks, because virtually all volcanic rocks have much more Cr than Ni (Gill 1981). In the case of sediments derived from a volcanic arc, for example, one would expect low concentrations of Cr and Ni with Cr/Ni ≈ 2.0 or greater (Garver and Scott 1995).

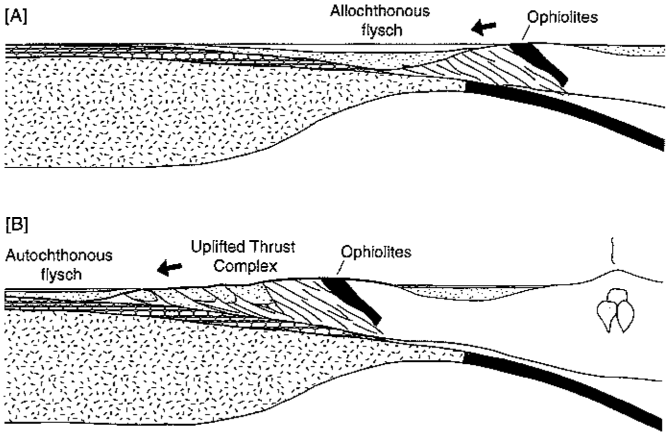

FIG. 5.—Inferred evolution of the Taconic orogeny, after Rowley and Kidd (1981). Although Rowley and Kidd (1981) drew this model for western New England, the general scenario is probably applicable to most of the northern Appalachians, with the notable exception, as they pointed out, that north of New England the forearc region was probably floored by extensive ophiolites. Note that the older flysch ("allochthonous" in [A]) is eventually incorporated into the deformed rocks at the leading edge of the orogen ("uplifted thrust complex" in [B]).

Cr and Ni Geochemistry as a Provenance Indicator

Our data suggest that elevated concentrations of both Cr and Ni in shale can be used to determine: (1) spatial distribution of ultramafic rocks in a source region and (2) the relative timing of uplift and erosional denudation. Our observations and analyses suggest that the grain size of the sediment is important in determining the Cr and Ni geochemistry of that sediment, and shale clearly provides a clear and systematic geochemical signature of this geochemically unique source. Much of the Cr in sandstone probably is in detrital chromite, which is more abundant, but in variable proportions, in sandstones (e.g., note the scatter of sandstone analyses in Figure 3). Hiscott (1984) reported relatively common detrital chromite in sandstones

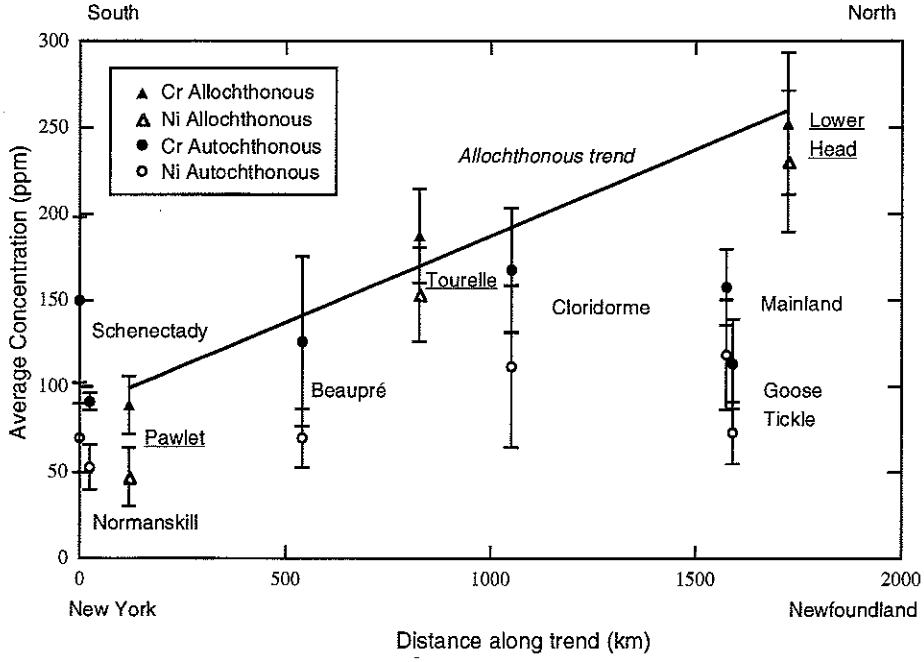

FIG. 4.—Average concentrations of chromium (filled symbols) and nickel (open symbols) in flysch (interbedded sandstone and shale) units along strike from New York to Newfoundland. Allochthonous units (triangles; unit names are underlined) show a much more systematic change than the autochthonous units (circles), which show much greater variability. The north-to-south trend in the allochthonous rocks is denoted by the solid regression line (fit to Cr). Error bars show the standard deviation of the average for each unit (see Table 1). Distance is measured relative to Albany, New York ("A" in Figure 1), along the frontal thrust zone northward to Newfoundland. Note that the Schenectady Formation has elevated chromium but not nickel; this is more typical of a volcanic provenance. See text for discussion.

with Cr values typically between 300–900 ppm, but in one case close to 4000 ppm. In fact, in sandstones from the same units we studied, Cr/Ni $>$ 4.0. In shale, the systematic covariation in Cr and Ni suggests that detrital chromite is not the main chromium-bearing phase. The concentrations of Cr and Ni in shale probably reflect incorporation of Cr and Ni ions to clay particles during weathering of ultramafic rocks containing chromite and Cr- and Ni-bearing pyroxene, olivine, and serpentine.

Where the Cr and Ni resides in the shale is an important but not completely resolved problem. The various Cr- and Ni-bearing phases in the Normanskill Formation (New York) were studied by Weber and Middleton (1961a, 1961b), who suggested that although chromite was present in both the clay-size fraction and the sand-size heavy-mineral fraction, most of the Ni was in the clay-size fraction. Likewise, Hiscott (1984) concluded that where Cr and Ni were adsorbed ions on clays, and when concentrations are high, there is a significant input of Cr and Ni from detrital ultramafic minerals and by the dissolved loads of rivers.

On the basis of work discussed above and that by Gibbs (1973, 1977), we suggest that Cr and Ni in shale probably are in the form of either detrital particles or adsorbed ions on particles—both of which are fundamentally influenced by source-area lithology. Gibbs (1973, 1977) showed that in large river systems the transport mechanism of the transition elements varies with individual elements and is not the same for Cr or Ni. He concluded, however, that the principal factor controlling the transport of these elements is the bedrock geology in the drainage basin.

Comparison of Cr/Ni ratios in ultramafic rocks to those in shale inferred to have been derived from ultramafic rocks provides an important clue to transport efficiency. Ultramafic rocks in ophiolites have Cr and Ni concentrations several orders of magnitude greater than most other intrusive and extrusive igneous rocks (Cr $\approx$ 2400 ppm; Ni $\approx$ 1500 ppm; Goles 1967) with a Cr/Ni $\approx$ 1.6. Shale from our data set with Cr and Ni concentrations above background values have average Cr/Ni ratios of 1.3–1.5, i.e., slightly lower than the average ultramafic rock; this may indicate that some Cr is preferentially excluded from shale, and detrital chromite in sandstones (Cr/Ni $\approx$ 4.0) may account for this deficit. Therefore, a likely scenario for transfer of detritus from an ultramafic-bearing source is that most Cr and Ni is preserved in clays, and that resistant chromite is preferentially fractionated into the sandstones.

We suggest that transfer of Cr and Ni into the fine-grained sediments derived from ultramafic-rich ($> \approx 10\%$) source regions is nearly complete, and that other Cr- and Ni-poor rocks in the source region dilute the Cr and Ni signal. Absolute concentrations should be much lower when dilution or mixing with sediment from Cr- and Ni-poor rocks is significant. Our results suggest that shales with high Cr and Ni concentrations have Cr/Ni ratios similar to those in ultramafic rocks. Therefore, we suggest that an important criterion for identifying shale with an ultramafic provenance is that Cr/Ni $\approx$ 1.4–1.6 and the concentrations are above background (N.A.S.C., for example).

If the transfer of Cr and Ni from source rocks to shale in a given sedimentary sequence was nearly complete, then the volume of ultramafic rocks in the source region can be estimated. For example, in this study we can make a rough approximation of the volume of ultramafic rocks in the source region using some simple assumptions. In our calculations we use the average Cr and Ni values from the various units and assume that the Cr and Ni in the shale was entirely derived from ultramafic rocks. For each unit, separate calculations for Cr and Ni are averaged to obtain an estimate of ultramafic rocks in the source. We calculate that the percentage of ultramafic rocks in the source was $\approx 13\%$ for the Lower Head Formation, $\approx 9\%$ for the Tourelle Formation, and $\approx 3.5\%$ for the Pawlet Formation. This trend (Fig. 4) has also been recognized in the Taconic foreland basin by other means, and our estimate for the Tourelle Formation is similar Hiscott's 7% estimate.

CONCLUSIONS

We have shown that Cr and Ni in shales record the geochemical signal of ultramafic rocks in a source region. Our scatter plot of Cr vs. Ni suggests that concentrations in shales vary systematically and provide a nearly unfractionated sample of the source region, in contrast to sandstones. We consider elevated values of Cr ($>$ ca. 150 ppm) and Ni ($>$ ca. 100 ppm), Cr/Ni $\approx$ 1.3–1.5 and a high correlation coefficient between Cr and Ni ($r \geq 0.90$) to be diagnostic of ultramafic rocks in the source region. Higher Cr/Ni ratios ($\approx$ 2.0 and greater) typify mafic-volcanic detritus; in these cases, Cr is linked to vanadium and titanium (see Garver and Scott 1995). Sandstones tend to have higher values of Cr than shales from the same units, presumably because of the presence of the resistant mineral chromite, whereas shales have a greater Ni concentration. This observation supports the suggestion by Weber and Middleton (1961a, 1961b) that Ni is principally derived from easily disintegrated pyroxene, olivine, and serpentine. Therefore, although unroofing of ultramafic rocks is reflected in the geochemistry of adjacent stratigraphic sequences, systematic sampling throughout an entire stratigraphic section is needed to delineate unroofing trends.

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