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THE PRESENCE OF OPHIOLITES IN TECTONIC HIGHLANDS AS DETERMINED BY CHROMIUM AND NICKEL ANOMALIES IN SYNOROGENIC SHALE: TWO EXAMPLES FROM NORTH AMERICA

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Shale from synorogenic deposits where ophiolites and their ultramafic component are known to have been in the source region were analyzed by Inductively Coupled Plasma Mass Spectrometry for their trace element composition in order to determine if the distinct geochemistry of the ultramafic rocks is transferred to the sediments. One hundred and thirty five shale samples and a few sandstone samples from foreland basin deposits of the Taconic collision zone (Ordovician) of the Appalachian mountain chain of eastern North America were analyzed. Additionally, some fifty samples of shale from pre- and synorogenic basin strata of a mid-Cretaceous (Albian-Cenomanian) collision zone in southern British Columbia were also analyzed. In each case, other studies [1–3] have shown that abundant detrital chromite and serpentinite in the interbedded sandstones were probably derived from the ophiolites in the collision zone that were known to have been thrust during orogenesis. All pre-orogenic shales show no Cr and Ni anomaly, but in each case, the shale from strata with interbedded chromite-bearing sandstones shows a distinct Cr and Ni anomaly. The samples showing the Cr and Ni anomaly have both Cr and Ni values between about 150–1000 ppm and a Cr/Ni ratio between about 1.2–1.5. A high correlation coefficient between Cr and Ni (>0.90) and correspondingly high correlation of both elements to cobalt, suggests derivation of these elements from ultramafic rocks. The Cr and Ni are probably absorbed onto clay particles or transferred to clay particles through cation exchange. We suggest that: 1) elevated concentrations of Cr and Ni; 2) high correlation coefficient between Cr and Ni; and 3) a Cr/Ni ratio of about 1.2 to 1.5 can be used to determine the presence of ultramafic rocks, and therefore presumably ophiolites, in a source terrane to rocks of unknown origin.

INTRODUCTION

Few lithologic assemblages intrigue geologists as much as ophiolites, which are widely thought to represent pieces of oceanic lithosphere [4]. Although ophiolites are rarely well preserved on land, they have long been known to mark fundamental boundaries between different petrotectonic assemblages, and a string of ophiolites is commonly interpreted as a suture zone between two terranes. Geochemically, the ultramafic rocks of an ophiolite assemblage are distinct because the concentrations of Cr and Ni are orders of magnitude greater than virtually any other rock [4].

Because ophiolites commonly mark suture zones, their importance in understanding the evolution of convergent margins cannot be overestimated. In collisional zones where ophiolites mark the suture zone between different terranes, the timing of ophiolite emplacement may be more or less synchronous with uplift, erosion, and deposition of the ophiolite-rich detritus into adjacent basins. Although many studies have concentrated on the provenance of sandstones, few workers (with the notable exception of Danchin [5]) have used shale as a provenance indicator for ultramafic rocks. The occurrence of detrital chromite in sandstones

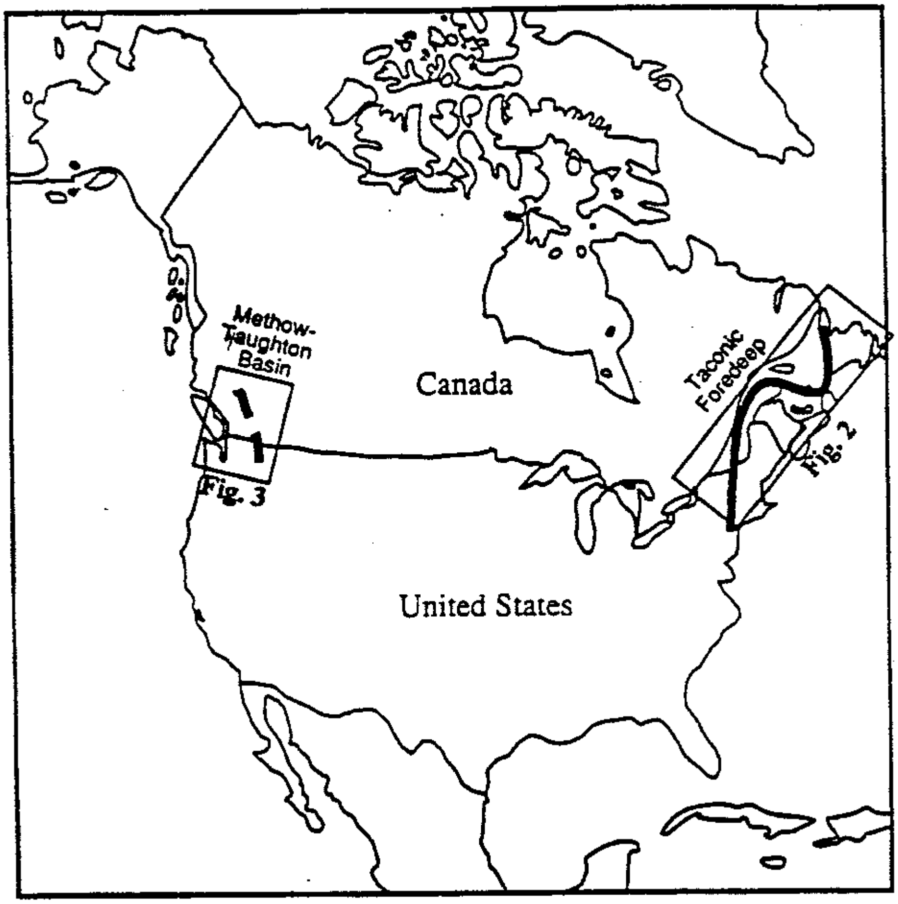

Fig. 1. Map showing the location of the study areas. One-hundred and thirty five samples of shale from flysch from the Taconic foredeep were analyzed from eastern North America, and fifty samples were analyzed from the Tyaughton basin in British Columbia. Both basins are interpreted to have had ophiolites as a significant component of the source region during sedimentation.

deposited during tectonic activity involving ultramafic rocks has been interpreted to signify the former existence of ultramafic rocks in source regions ([1, 3, 6] among others).

To test the idea that Cr and Ni in shale can be used as a provenance indicator of ophiolites in adjacent highlands, we examined the shale of the Ordovician Taconic foredeep in eastern North America [7] and the synorogenic strata of the Methow-Tyaughton basin in western North America [8] (Figs. 1, 2, 3). These rocks were selected because sandstones in the synorogenic strata contain abundant chromite and the provenance of these sandstones (and some conglomerates) suggests that ophiolites were present in the source regions. In eastern North America, we analyzed shale samples of synorogenic strata from seven principal localities from western Newfoundland to eastern New York, a traverse of about 2000 km along strike (Fig. 2). In western North America, we analyzed some fifty samples from a limited geographic area, but we sampled strata that were deposited from the Upper Triassic to the mid-Cretaceous (Albian-Cenomanian).

COLLISION OF THE TACONIC ARC (EASTERN NORTH AMERICA)

The Ordovician tectonism of the Appalachian Mountains (Fig. 2) is interpreted to be the result of a collision of the west-facing Taconic arc with the eastern passive margin of North America; the surface expression of the Middle to Late Ordovician Taconic orogeny is interpreted to have been characterized by ophiolite obduction and imbricate thrusting within a westward-advancing orogenic wedge and coeval deposition in an adjacent foredeep [2, 9–16]. The sedimentary record of collision is marked by widespread deposition of

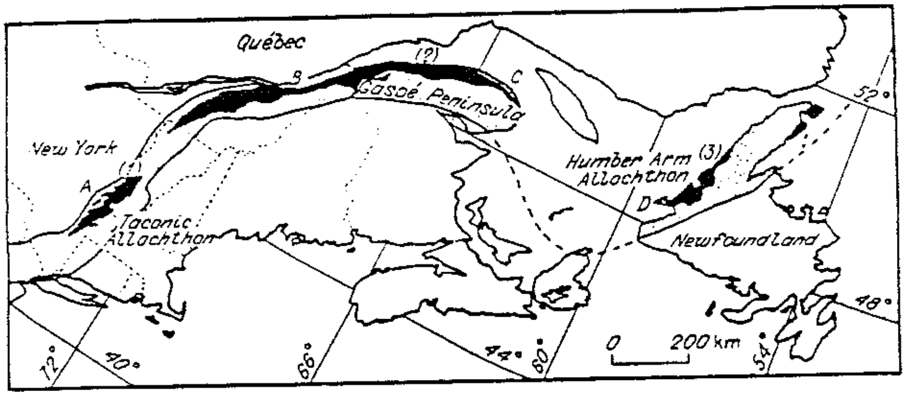

Fig. 2. Map showing the location of deformed rocks of the Taconic orogeny which consists of allochthonous rocks (shown in black) and autochthonous rocks that structurally underlie the allochthonous thrust sheets (shown in stipple). The strata of the autochthonous foreland basin are exposed and were collected from sites A-D; these basin strata extend westward and northward from the deformed belt and rest on cratonal North America. Allochthonous strata were collected from sites 1–3.

flysch in which immature sandstones were derived from emergent highlands. Detrital chromite and ultramafic detritus is present in many of these sediments [1, 2].

COLLISION OF THE INSULAR TERRANE (WESTERN NORTH AMERICA)

The Methow and Tyaughton basins are located between the Insular terrane and what was the western edge of North America (Fig. 3). A major episode of mid-Cretaceous (ca. 100 to 90 Ma) contractional deformation and metamorphism is well established for rocks that occur along the boundary of the Insular and North America [17–20 and references therein]. Most workers feel that this period of compressional tectonics was driven by the collision of the Insular terrane against the western margin of North America although the timing of initial juxtaposition is controversial [3].

The Tyaughton basin includes a 3-km-thick section of Albian-Cenomanian strata that overlie both highly deformed Mississippian-Jurassic rocks of the Bridge River terrane (an accretionary complex) and Triassic-Jurassic arc-related rocks of the Cadwallader terrane [3, 21 and references therein]. The Methow and Tyaughton basin first shared a common history in the Early Albian (ca. 110 Ma) when the Bridge River terrane and the Shulaps ophiolite were uplifted during contraction [3, 20, 21]. Chert lithic detritus (Cherty petrofacies) in the Tyaughton basin was east-derived and records the erosion of the Bridge River terrane and the Shulpas ophiolite that were imbricated and thrust in the Albian-Cenomanian [3]. The Cherty petrofacies, therefore, represents the erosion of uplifted miniterranes (mainly the Bridge River terrane and the Shulpas ophiolite) caught between the Insular terrane and North America during collision. It is widely known that the mid-Cretaceous strata record collision and the thrusting of ophiolites; the older strata were sampled for comparison and to test whether the Middle Jurassic was a time of ophiolite obduction as suggested by some workers [22].

METHODS

A total of 135 shale samples were collected and analyzed from the flysch of the Taconic foredeep, and about 50 shale samples were collected and analyzed from strata of the Tyaughton basin. The details of the sample locations, and the preparation techniques are summarized in several works [8, 23–26]. The powdered rock samples were weighed, ignied at 950 °C, and dissolved using HF and HNO_3. The trace elements 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 (model PQ2) in the Geology Department at Union College. The United States National Bureau of Standards (NBS) sample 688 was used for the machine calibration. NBS 688 is a basalt with 250 ppm V, 332 ppm Cr, 49.7 ppm Co, 150 ppm Ni, 96 ppm Cu, and 1.168 wt.% Ti [27]. Each sample was run in duplicate and all data used in this study represent the average of the two duplicates. The

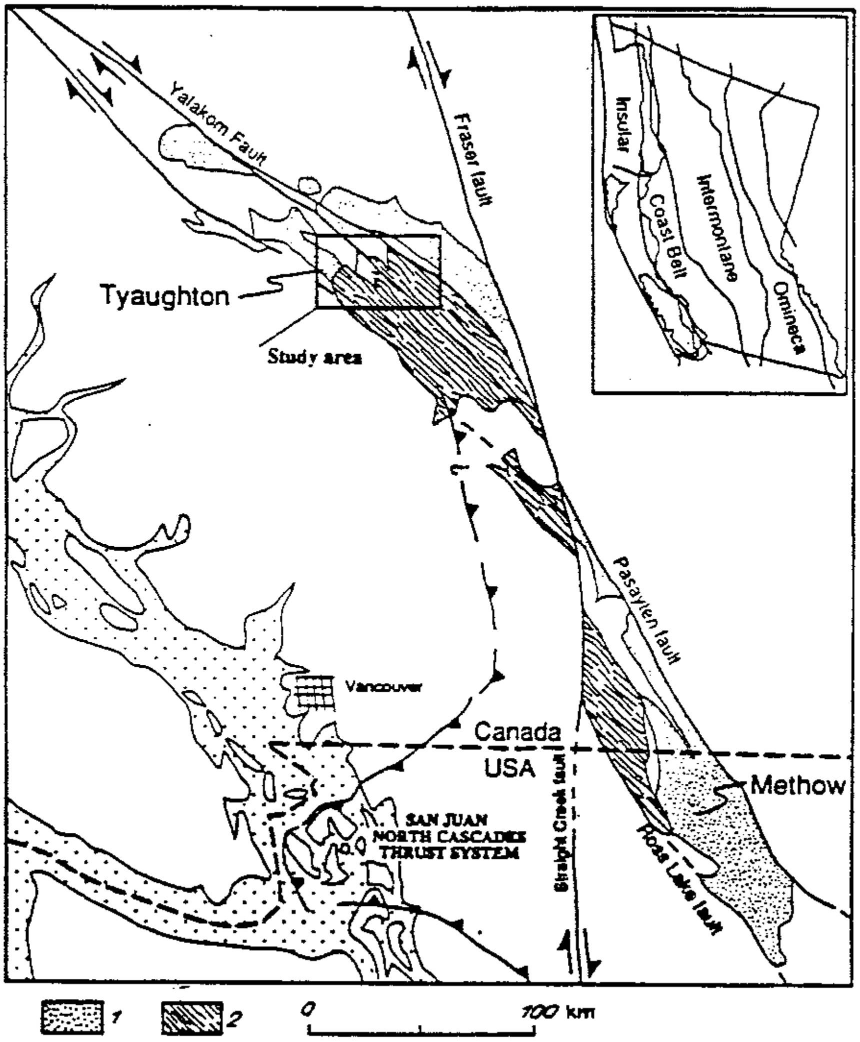

Fig. 3. Map showing the location of the mid-Cretaceous deposits of the Methow and Tyaughton basin in British Columbia (Canada) and Washington (USA). These rocks are inferred to record the sedimentological and structural events associated with the accretion of the Insular belt to the Intermontane belt (see inset) in the mid-Cretaceous (Albian-Cenomanian). The study area includes the extensive overlap sequence that records this collision, as well as an oceanic complex that was deformed and thrust during accretion. Ophiolitic rocks were thrust with this oceanic complex. *1* — sequence of Albian — Cenomanian overthrust; *2* — Bridge-River oceanic complex.

percent error was calculated for the average between all samples and their duplicates and the average relative deviation for the mean values is 3 % for Cr and Ni.

RESULTS

The data from all shale samples (185 total) are plotted in Figure 4 which shows a simple regression line though the data. The slope of this line is about 1.2 which is assumed to be the "natural"ratio of Cr/Ni in shale derived from ultramafic rocks. The relationship between all shale and sandstone samples from the Taconic foredeep and sandstones from the same rock units analyzed by Hiscott [1] are shown in Fig. 5. Also plotted on Fig. 5 is the North American Shale Composite (N.A.S.C. value is where the lines cross on the figure) which is thought to be representative of "average"crustal rock in North America [28] although these values are

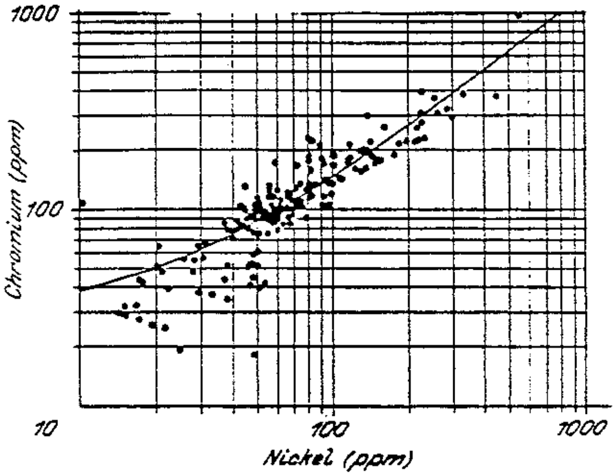

Fig. 4. Chromium versus nickel for all shale from sediment from both the Taconic foredeep (eastern North America) and the Tyaughton basin (western North America). Elevated values of Cr and Ni are from those units that are known to have a ultramafic component in the source region. The slope of the line (which is straight. but appears curved on this log-log plot) is about 1.2; suggesting that the Cr/Ni ratio in shale that had a partial source of ultramafic rocks should have this value.

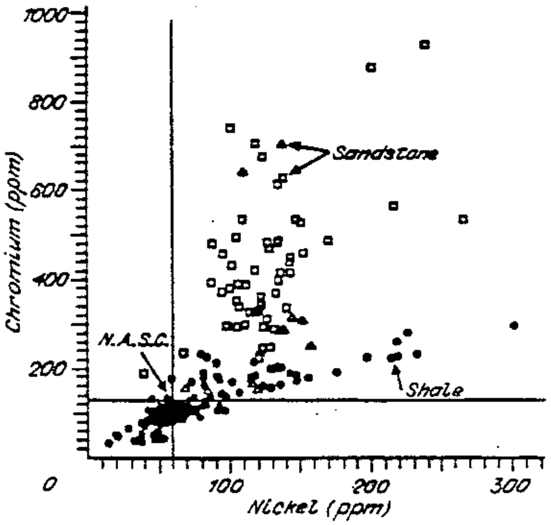

Fig. 5. Chromium versus nickel for all shale (solid circles) and sandstone (open triangles) samples of the sediments from the Taconic Foredeep. Additionally, sandstone analyses of Hiscott [2] are shown (open squares). Although Hiscott's study included many other units, this graph includes only those formations considered in this study. The North American Shale Composite (N.A.S.C.; vertical and horizontal lines) has average values of chromium (125 ppm) and nickel (60 ppm).

controversial. It is important to note that the sandstone samples show a wide scatter; one point (not plotted) had ~ 4000 ppm Cr [1]. These results suggest that shale is a more homogeneous representation of the source region, and that sandstones have a greater concentration of chromite which is a mineral that is relatively resistant to chemical or mechanical breakdown. The average Cr and Ni concentrations for strata of the Tyaughton basin are shown in Fig. 4. This diagram clearly shows a pronounced Cr and Ni anomaly in the mid-Cretaceous strata.

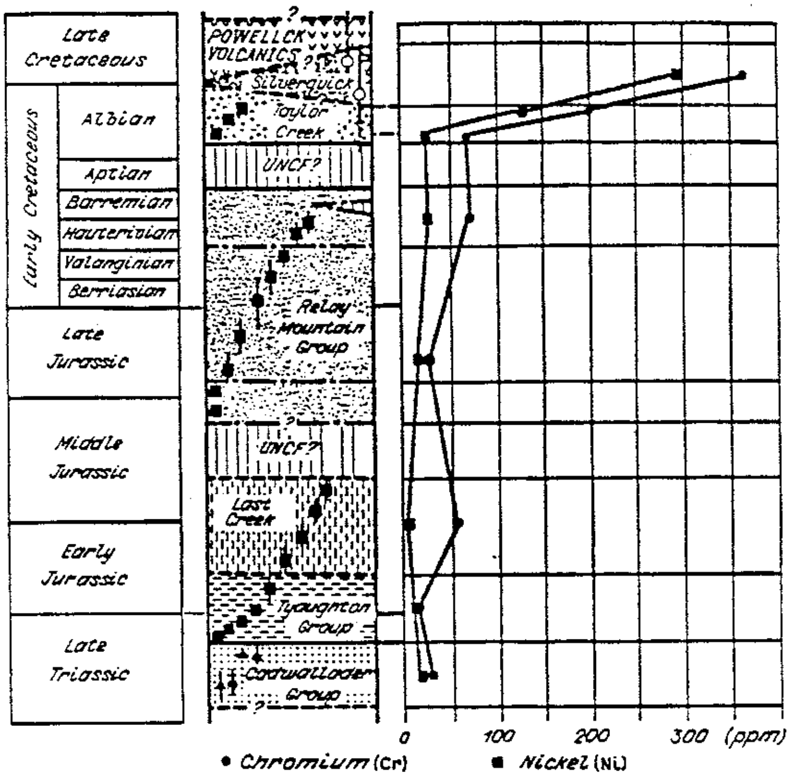

Fig. 6. Stratigraphy of the Tyaughton basin showing average Cr and Ni values for all units analyzed. Symbols on the stratigraphic column represent fossil control which is excellent for this sequence (triangle – conodonts; squares – marine macrofossils; open circles – plant fossils). Cr and Ni values are the average of four analyses for each unit (except the Taylor Creek Group which is divided between the upper and lower sections). Note that the Jurassic strata show elevated Cr but not Ni; this trend probably represents Cr from a volcanic source. Thrusting of ophiolites in the Albian results in a significant anomaly in both Cr and Ni. Figure modified from Garver [29].

DISCUSSION

Elevated values of both Cr and Ni in shale and sandstone (Fig. 4, 5) are interpreted to reflect ultramafi rocks in the source region. Higher concentrations of Cr in sandstone and relative enrichment of Ni in shal presumably indicates the derivation of these elements from different mineral phases in ultramafic rocks. Th variation of Cr and Ni in shale is more systematic and occurs within a relatively narrow range as compare with the variation in sandstones from the same units (Fig. 5). Background values of Cr and Ni are fairly we estimated by the North American Shale Composite (N.A.S.C) [28] values which are Cr (125 ppm) and N (60 ppm) (Fig. 2) [28], with a Cr/Ni ratio of about 2.

Our observations and analyses suggest that the grain size of the sediment plays an important role i determining its Cr and Ni geochemistry. Much of the Cr in sandstone probably occurs as detrital chromite which is a relatively resistant mineral and is therefore more abundant in coarse clastic rocks. Sandstones c the Taconic flysch (most data from Hiscott [1]) have Cr/Ni ratio that is greater than 4.0. On the other hanc the Cr/Ni ratio in shale in the Taconic flysch is about 1.2. In ultramafic rocks, Ni is incorporated into pyroxen and olivine, both of which are nonresistant minerals and are easily broken down mechanically and chemicall whereas much, but not all, of the chromium occurs as chromite. Ultramafic rocks in ophiolites hav concentrations of Cr and Ni that are several orders of magnitude greater than most other intrusive and extrusiv igneous rocks (ca. Cr = 2400 ppm; N = 1500 ppm [26]). Shales containing concentrations of Cr and Ni c two to three times background values in a ratio of about 1.2 to 1.6 (the range for both study areas) ar interpreted to be derived from ultramafic rocks. The ratio of Cr/Ni in ultramafic rocks is about 1.6 [4]. Th ratio between Cr/Ni in ultramafic rocks (1.6) and shale clearly enriched in both Cr and Ni (Cr/Ni = 1.2 to 1.6) is very close; the difference is probably a result of the resistant chromite grains being preferentially enriched in the sandstones as opposed to the shale. We have found that Cr/Ni ratios greater than about 2.0 are characteristic of a source terrane dominated by volcanic rocks. Cr/Ni ratios less than about 1.2 are uncommon.

In the area of the Tyaughton basin, it is controversial as to the timing of terrane juxtaposition. There is little question that the mid-Cretaceous was a time of intense deformation. It is uncertain, however, if an earlier tectonic event (Middle Jurassic) occurred and involved ophiolite obduction. To test this possibility, we analyzed several shale samples from each unit of the Tyaughton basin sequence and found that only the Albian strata show a significant Cr and Ni anomaly (Fig. 4). Elevated Cr but not Ni in the Lower to Middle Jurassic strata probably indicate a volcanic input because volcanic rocks tend to have a relatively high Cr/Ni ratio and the strata are rich in volcanoclastic detritus. This finding indicates to us that if the Jurassic was a time of terrane accretion, ophiolites were not present in the suture zone.

CONCLUSIONS

From this study, we can make the following observations concerning the occurrence of Cr and Ni in shales and sandstones that are interpreted to have been derived from a source region with a significant component of ophiolites: 1) Cr and Ni can be used as a provenance indicator of ultramafic rocks in shales (and presumably slates and metapelites). Concentrations in shales vary systematically, and are probably a more homogeneous representation of the source region as compared to sandstones; 2) Elevated values of Cr (greater than ca. 150 ppm) and Ni (greater than ca. 100 ppm) and a Cr/Ni ratio of about 1.2 to 1.6 and high correlation coefficient ($r \geq 0.90$) are most likely indicative of ultramafic rocks in the source terrane; 3) Sandstones tend to have higher values of Cr, presumably due to the presence of the resistant mineral chromite, whereas shales from the same units have a greater concentration of Ni and a lower concentration of Cr but are much more homogeneous. In sum, we suspect that these findings can be used to determine the timing of uplift and erosion of ophiolites by sampling a stratigraphic section that records a collision event, or to test strata of unknown provenance for an ultramafic component to the source region.

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