Chapter 13

Mineral control of minor, trace and rare earth elements during black shale weathering at near-neutral pH

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Abstract

Mineral dissolution and alteration commonly influence the concentration of chemical species in natural water systems and consequently on water quality. This research looks at the role of mineral-water interactions during black shale weathering in influencing the chemical composition of streams and groundwaters with emphasis on minor and trace elements and the rare earth elements (REE). We performed batch weathering experiments under standard laboratory conditions standard laboratory conditions (standard ambient temperature ($\sim 25^{\circ}$C) and pressure (~ 100 kPa)) using three black shale samples from the Utica shale magnafacies of Quebec, Ontario and New York using buffered weathering solutions at pH 5 to determine the mineralogical controls of dissolved metal concentrations. R-mode factor analysis was used to describe the relationship among different elements (Ti, V, Cr, Ni, Zn, As, Sr, Ba, Th, U and the REE) in the weathering fluids. Five factors were extracted that accounted for 95% of the variance within the data. We interpret these five factors as representing the breakdown products of four major mineral phases (phosphates, carbonates, silicates and sulfides) in the black shale as well as the breakdown of organic matter. Our results also suggest that during weathering of black shales, the REE are fractionated leading to enrichment of the MREE (Sm-Dy) and HREE (Ho-Yb) relative to the LREE (La-Nd). We also observed that the average concentration of minor and trace elements and the REE in solution was highest during the first 24 h of reaction and decreased slowly with time. We interpret the changes in dissolved metal concentrations as the result of rapid breakdown or dissolution of easily weathered mineral phases, partial oxidation of organic matter and to the desorption of metals that are loosely bound to exchange sites on clay minerals. The decrease in metal concentration with time may be related to processes

such as precipitation of secondary phases and sorption as well as dissolution of easily weathered mineral phases.

13.1. Introduction

Variations in stream water composition in many areas have been attributed to different weathering rates of the surrounding geological materials (Horton et al., 1999; Pretti and Stewart, 2002). Natural weathering of black shale may lead to increased abundances of dissolved minor and trace elements in solution, some of which at sufficient concentrations may impair water quality (Isaacs et al., 1999; Coveney, 2004). The minerals that weather to release these elements (phosphates, carbonates, sulfides and silicates) including organic matter are associated with the host rock and may weather at varying rates. Most laboratory studies of chemical weathering have looked at the weathering of pure mineral phases (Stumm, 1990; Lasaga et al., 1994; Zhang and Bloom, 1999; White and Brantley, 2003). Laboratory studies of chemical weathering of whole rocks to study how minerals weather in concert and the contribution of individual minerals to the concentration of chemical species in natural systems are few. Most experimental work to simulate chemical weathering of rocks in the field has resulted in mineral weathering rates in the laboratory being several orders of magnitude higher than those experienced in the field (Malmstrom et al., 2000; White and Brantley, 2003). Several hypotheses have been advanced to explain the observed differences between mineral weathering rates in the laboratory and in the field. Despite the availability of data on the weathering rates of pure minerals in the laboratory and extension to field weathering rates, it remains unclear how minerals weather in concert in whole rocks especially in fine-grained sedimentary rocks rich in organic matter. Because the weathering of a multimineralic rock such as black shale involves a complex interplay of processes such as oxidation, dissolution, precipitation and hydrolysis, it is important for any conclusive study to involve detail mineralogical studies of the whole rocks, mass balance calculations to determine the percentage of individual mineral contribution to the total elemental concentration in solution and consequently to use the data in modeling field weathering of black shale and release of trace metals to neighboring systems.

Field studies of black shale weathering have shown that chemical breakdown of these rocks may lead to elevated concentrations of trace metals and increased acidity in associated aquatic systems (Piper and Isaacs, 1995; Lee et al., 1998; Peucker-Ehrenbrink and Hannigan, 2000; Dalai et al., 2001; Coveney, 2001; Tuttle et al., 2001; Tuttle and Breit.,

2004). Owing to a combination of reduced minerals like pyrite, oxidizable organic matter and easily weathered minerals like calcite and the presence of high levels of metals in many black shales, these rocks upon exposure to surface conditions (oxygen- and moisture-rich conditions), may breakdown easily releasing high levels of associated trace metals. Additionally, because black shales are made up mostly of fine-grained clay-size particles, the minerals provide a large surface area to chemical attack.

Primary as well as secondary minerals in black shale differ in their degree of resistance to weathering. Mineral weatherability has been studied by Loughnan (1969) and Carrol (1970). Berner and Berner (1996) and Drever (1997) have compiled tables of mineral weatherability based on their resistance to weathering. Bearing in mind the mineralogy of our samples (section "Methods"), the weatherability of minerals will increase in the order of clay minerals < biotite < Ca plagioclase < calcite < pyrite. However, it is important to note that this order depends on other factors including particle grain size or surface area of minerals exposed as well as the presence or absence of crystal defects in minerals. The black shale samples used in this study are made up mostly of clay-sized particles, so the problem of grain size in determining mineral dissolution rates is not critical. However in organic rich sediments, the breakdown or oxidation of organic matter may play an important role in determining the rate of primary mineral dissolution and release of trace metals (Stillings et al., 1996; Drever and Stillings, 1997; Zhang and Bloom, 1999). Zhang and Bloom (1999) suggested that organic anions tend to increase the rate of silicate weathering because these anions are capable of forming complexes with framework metals thereby enhancing both the solubility of the metals and the dissolution of minerals.

This chapter reports the results of a two-week weathering experiment to determine the mineral control of minor, trace and rare earth elements (REE) during black shale weathering using buffered weathering solutions at pH 5. This study involves a controlled laboratory leaching experiments of three black shale samples from the Utica Shale Magnafacies (USM) of Quebec, Ontario and New York. Specifically, we looked at the mineral control of minor and trace elements including the REE during weathering of a fine-grained multimineralic rock (black shale) at pH 5. We investigated the behavior of the following elements including Ti, V, Cr, Ni, Zn, As, Sr, Ba, Th, U and the REE (La-Lu) during an experimental period lasting 13 days (312 h). Here, we look at how different minerals in black shale breakdown together and which minerals exert greater control on the chemistry of the resulting weathering solutions. Our objective was to study elemental association of most easily weathered minerals in black

shales of different grades of thermal maturity. We used R-mode statistical analysis to describe the relationship among Ti, V, Cr, Ni, Zn, As, Sr, Ba, Th, U and the REE in order to determine the dominant mineral control of these elements in solution. The results presented in this chapter are in no way conclusive about how minerals weather in concert and the contribution of individual host mineral to the elemental content in solution during black shale weathering. However, this study provides important baseline data critical in understanding the contribution of easily weathered minerals in black shale to the composition of chemical species in natural systems associated with black shale. The study sheds some light on the major control (mineral) on the release of minor and trace elements during chemical breakdown of black shale at pH 5.

13.2. Geological setting

In this study, we focused our attention on the release of Ti, V, Cr, Ni, Zn, As, Sr, Ba, Th, U and the REE during weathering of time correlative Middle Ordovician Utica Shale magnafacies (USM) of Quebec, Ontario and New York (Hannigan and Basu, 1998). These units were deposited in the Taconic Foreland Basin and have been constrained in time by graptolite biostratigraphy and bentonite chronostratigraphy. There is evidence that these units share a common provenance (Lehmann et al., 1995). The magnafacies thermal grade varies geographically; Quebec (thermally immature: T_{max} 20–50°C), Ontario (thermally mature: T_{max} 50–140°C) and New York (thermally post-mature: T_{max} 200°C) Hannigan and Basu (1998). We selected rocks of different grade of thermal maturity not only to show how minerals in black shale weather in concert but also to investigate the effect of thermal maturation on the mobility of minor and trace elements, especially the REE during chemical breakdown of these rocks.

13.3. Methods

13.3.1. Sample selection and preparation

Samples used in this study were obtained from drill cores. Samples were carefully selected to include samples with similar amounts of organic carbon, mineral carbon and total sulfur. The core samples were broken into smaller fragments with a hammer. We selected rock fragments that ranged between 1 and 2 mm in diameter and weighed about 2.5 g of each sample into a 100 ml PTFE bottle. We submerged the rock fragments in

deionized water (18.3 M Ohm) and subjected them to ultrasound for about 20 min to remove fine surface particles. This exercise was repeated five times using fresh deionized water. It is worth mentioning that before the end of this process the rock fragments were reduced further into even smaller size fractions because of the fragile nature of these fine-grained sediments. Because of the brittle nature of the samples and the minute sizes of mineral grains, it was difficult to estimate the surface area exposed to weathering. Isolation of the $<2\,\mu m$ clay-size fraction was done according to the method of Poppe et al. (2001). A fraction of the sample was pulverized ($<63\,\mu m$) and used to isolate the clay fraction. We used acetic acid to leach carbonate minerals associated with our samples and sodium pyrophosphate was used to put the clay fraction into suspension. The supernatant solution containing the $<2\,\mu m$ clay fraction was siphoned off and centrifuged at high speed (~3000 rpm) for 10 min to obtain the clay fraction. This fraction was mounted on glass slides and air dried before carrying out X-ray diffraction analysis.

13.3.2. Dissolution experiments

Batch weathering experiments have been applied by other workers in the study of mineral dissolution (Holdren and Berner, 1979; Stidson et al., 1998; Zhang and Bloom, 1999). These authors used initially reacted samples to overcome the effects of rapid initial dissolution, which is usually an artifact of sample pre-treatment (surface strain, ultrafine particles and high-energy crystal defects). Our samples were not pre-treated because of their fragile nature and concerns with easily weathered minerals like carbonate and sulfides. Because our study was concerned about the contribution of easily weathered minerals to the composition of chemical species in solution, we think pre-treatment would have significantly altered the composition of sulfides and carbonate minerals. However, to curb the effects of ultrafine particles on dissolution rates, our samples were treated as outlined in section "Sample selection and preparation" (washed several times in deionized water in an ultrasound bath). We prepared buffer solutions pH 5 using trace metal grade reagents. To each pre-weighed 2.5 g washed samples, we added 25 ml of buffered solution (pH 5) in a 100 ml PTFE bottle. After adding 25 ml of the buffered weathering solution to each sample, the bottles were capped and placed on a Lab-Line® orbital shaker at low speed through the whole length of the experiment (13 days). The dissolution experiment was carried out under standard laboratory conditions (standard ambient temperature ($\sim25^{\circ}C$) and pressure (~100 kPa)). At various times during the experimental period (24, 48, 96, 144, 168, 264, 288 and 312 h) we extracted the

weathering solutions for chemical analysis. Each time we obtained a sample, the entire weathering solution was emptied into a clean 100 ml PTFE bottle and the solid sample was washed using deionized water before adding fresh buffer solution (25 ml). By replacing the solution each time we collected a sample, our intention was to minimize oversaturation of the weathering solution and the precipitation of secondary mineral phases. The extracted solution was filtered through 0.45 μm millipore microfilter and stored in a refrigerator at 4°C for chemical analysis.

13.3.3. Analytical methods

Minor, trace and REE concentrations were measured by dynamic reaction cell inductively coupled plasma mass spectrometry (DRCII ICP-MS; PerkinElmer) following EPA 200.8 method (USEPA, 1991). We prepared standards in a linear range from 1 to $100 \, \text{mg} \, \text{l}^{-1}$. Each sample and standard contained $40 \, \text{ug} \, \text{l}^{-1}$ ^{115}In and ^{209}Bi internal standards. USGS SDO-1 (Ohio Devonian shale sample) (Kane et al., 1990) was digested and prepared in similar fashion and analyzed alongside samples and blanks to ensure accuracy of measurements. Elemental concentrations were within 5–7% of the reported values of these standards. Relative standard deviations for sample concentrations are better than 5% for all analytes.

Clay analyses were carried out at Arkansas State University using Rigaku X-ray diffractometer operated at 40 kV and 20 mA with CuKα radiation following the method of Moore and Reynolds (1989) on isolated clay size ($< 2 \, \mu\text{m}$) fraction mounted on glass slides. Major elements analyses was carried out at the SGS analytical laboratories in Ontario, Canada using X-ray fluorescence spectroscopy (method XRF100) with lowest detection limits of 0.1% for all majors and loss on ignition. Total carbon and total sulfur analysis was carried out using the Leco analyzer. Inorganic or mineral carbon was done by coulometry. Total organic carbon was estimated as the difference between total carbon and inorganic carbon.

13.3.4. Statistical approach

We subjected the geochemical data to statistical analyses (R-mode factor analysis) to study the controls of soluble elemental composition in the weathering fluids (Reeder et al., 1972). Factor analysis is a multivariate technique designed to analyze the interrelationships within a set of variables. Factors are constructed such that the overall complexity of data is reduced based on the interdependencies of the variables considered. The statistical package Minitab (Minitab for Windows 95/98/2000 and NT

Upgrade Version 13.30 by Minitab Inc.) was used for the analysis. Factor analyses present us with a set of factors that are used to explain the variance in the data collected. The number of factors considered was small enough to allow reasonable interpretation of our data. Based on the number of factors given, we used these factors to explain the source of all elements considered. Elemental association gives us information about possible controls of metal release during breakdown of the major easily weathered minerals. Loadings represent how each factor is associated with a particular variable and have numerical values that range between -1 and $+1$. Factors were adjusted using a varimax rotation. Varimax rotation is preferred because it ensures that one variable has high loading only on one factor and low or no loading on other factors (Reeder et al., 1972). Interpretation of the factors is based on rotated factors and rotated factor loadings.

13.4. Results

13.4.1. Mineralogy of samples

Earlier mineralogical studies by Hannigan and Basu (1998) revealed that the Utica shale samples are made up mainly of clay, 69%; quartz, 14%; calcite, 13%; K-feldspar; plagioclase–feldspar and biotite all constituting about 1% and diagenetic pyrite making up $<0.5\%$ in most of the samples. Clay mineralogical analysis revealed that the major clay minerals in the Utica shales include illite, smectite, mixed layer illite/smectite and minor amounts of chlorite and kaolinite (Hannigan and Basu, 1998). Mineralogical analysis of the samples used in this study support earlier results obtained by Hannigan and Basu (1998). The major clay minerals in our samples include illite, mixed layer illite/smectite, quartz and minor amounts of kaolinite (Fig. 13.1). Average organic carbon content in these shales is about 2 wt%. The organic matter is made up mostly of marine planktonic material since these rocks were deposited some 420 Ma ago before the proliferation of vascular land plants. The samples selected for this study contain similar amounts of organic carbon, total sulfur and inorganic carbon. Average organic carbon content in the samples was 5.2 wt%, total sulfur averaged 1.20 wt% and mineral carbon averaged 4.20 wt%. Average major oxides composition of the samples was $SiO_2 = 63.97$ wt%, $Al_2O_3 = 12.66$ wt%, $CaO = 3.42$ wt%, $MgO = 3.03$ wt%, $Na_2O = 1.34$ wt%, $K_2O = 2.28$ wt%, $Fe_2O_3 = 4.69$ wt%, $MnO = 0.09$ wt%, $TiO_2 = 0.51$ wt%, $P_2O_5 = 0.17$ wt%, $Cr_2O_3 = 0.03$ wt% and $LOI = 11.70$ wt%. The chemical index of
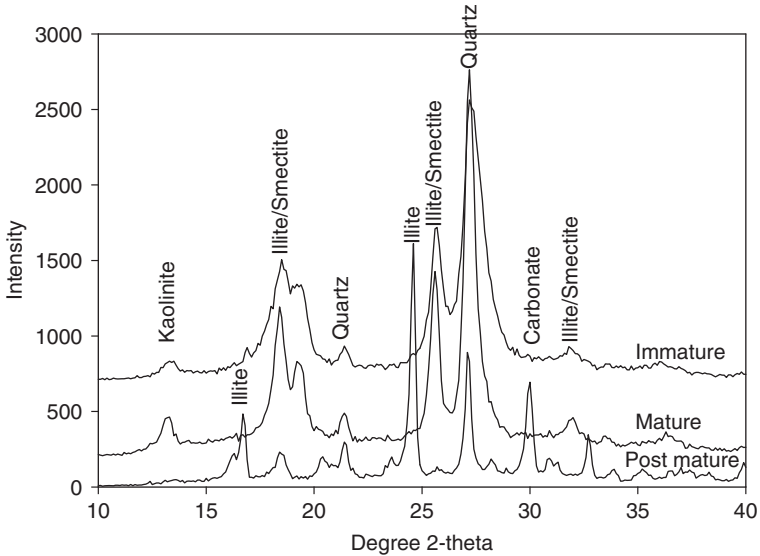
Figure 13.1. X-ray diffraction patterns of isolated clay-size fraction (air-dried) of thermally mature, thermally immature and thermally post-mature samples.

alteration (CIA) and chemical index of weathering (CIW) were computed from major element data as follows (Nesbitt and Young, 1982):

$$CIA = (Al_2O_3/(Al_2O_3 + Na_2O + K_2O + CaO))*100\% \text{ and}$$
$$CIW = (Al_2O_3/(Al_2O_3 + Na_2O + CaO))*100\%$$

The average CIA and CIW values were 64.26 and 72.67, respectively.

13.4.2. Rare earth elements (REE)

REE concentrations in weathering solutions are presented in Table 13.1. The concentrations of REE in the weathering fluids are low but significantly higher than the concentration of REE in natural waters. In ocean waters, the concentration of REE is < 10 ppt and about 200 ppt in river waters (Elderfield and Greaves, 1982; Taylor and McLennan, 1988). The sum of REE in the weathering fluids ranges from 2 ppb to 2 ppm. In the thermally immature sample, the highest REE concentration was observed after 24 h of reaction time. This concentration decreased to about 21 ppb after 288 h of reaction and increases to about 1 ppm at 312 h. In the thermally mature sample, the highest concentration of REE was observed during 144 h of reaction. In this sample, after 24 h of reaction the sum of

Table 13.1.   Minor, trace and REE concentration in samples collected over 312-h reaction period

Analytes	TI 24	TI 48	TI 96	TI 144	TI 168	TI 264	TI 288	TM 24	TM 48	TM 96	TM 144	TM 168	TM 264	TM 288	TM 312	TPM 24	TPM 48	TPM 96	TPM 144	TPM 168	TPM 264
Sr	60.189	12.368	4.341	1.497	0.711	0.575	0.567	16.289	13.725	9.374	7.116	2.022	1.598	0.850	0.569	24.047	21.970	20.082	27.786	26.321	20.768
Ba	37.398	15.520	8.407	3.343	1.594	1.033	0.987	0.853	1.610	1.217	0.944	0.432	0.295	0.203	0.455	3.914	3.519	3.154	4.412	3.329	2.336
Ti	0.949	0.768	0.440	0.215	0.204	0.700	0.670	0.830	1.000	0.427	0.786	0.392	0.277	0.320	0.279	0.686	0.696	0.530	0.780	0.987	0.648
V	0.066	0.059	0.045	0.025	0.030	0.025	0.089	0.026	0.031	0.019	0.035	0.039	0.037	0.043	0.043	0.016	0.020	0.008	0.022	0.125	0.011
Cr	0.240	0.265	0.238	0.177	0.200	0.358	0.479	0.201	0.268	0.112	0.237	0.170	0.142	0.182	0.233	0.194	0.268	0.202	0.354	0.288	0.239
Ni	0.748	0.769	0.535	0.267	0.341	1.139	1.450	0.847	1.253	0.327	0.934	0.376	0.284	0.311	0.511	0.593	0.928	0.472	0.981	0.555	0.688
Zn	0.778	0.637	0.437	0.261	0.235	0.257	0.460	0.108	0.166	0.022	0.135	0.078	0.045	0.066	0.147	0.194	0.202	0.087	0.196	0.271	0.111
As	3.188	4.718	3.341	1.688	2.639	6.845	14.283	4.130	7.375	0.157	4.371	1.855	1.358	3.549	5.258	2.385	5.936	0.964	5.433	4.195	1.348
La	0.168	0.100	0.074	0.037	0.027	0.013	0.076	0.255	0.087	0.176	0.415	0.184	0.116	0.074	0.141	0.003	0.004	0.005	0.012	0.056	0.006
Ce	0.404	0.266	0.205	0.132	0.096	0.015	0.230	0.478	0.115	0.330	0.781	0.406	0.282	0.185	0.503	0.006	0.007	0.012	0.017	0.185	0.013
Pr	0.060	0.034	0.029	0.015	0.012	0.007	0.035	0.065	0.016	0.042	0.098	0.054	0.040	0.029	0.087	0.001	0.002	0.001	0.005	0.026	0.002
Nd	0.296	0.168	0.137	0.076	0.059	0.034	0.193	0.262	0.068	0.167	0.389	0.221	0.177	0.134	0.487	0.004	0.012	0.006	0.025	0.119	0.010
Sm	0.124	0.065	0.059	0.027	0.027	0.026	0.094	0.073	0.028	0.034	0.096	0.050	0.035	0.038	0.169	nd	0.011	nd	0.016	1.044	0.003
Eu	0.041	0.020	0.019	0.007	0.008	0.008	0.025	0.018	0.008	0.008	0.023	0.011	0.007	0.009	0.039	0.001	0.004	nd	0.005	0.011	0.001
Gd	0.253	0.118	0.101	0.045	0.039	0.032	0.106	0.131	0.043	0.074	0.174	0.089	0.061	0.054	0.190	0.008	0.016	0.008	0.023	0.058	0.011
Tb	0.024	0.012	0.012	0.005	0.006	0.004	0.014	0.014	0.005	0.007	0.019	0.009	0.006	0.007	0.022	nd	0.002	nd	0.002	0.007	nd
Dy	0.132	0.066	0.064	0.028	0.026	0.017	0.067	0.083	0.026	0.048	0.118	0.059	0.037	0.033	0.106	0.001	0.007	nd	0.010	0.035	0.002
Ho	0.026	0.012	0.013	0.005	0.006	0.004	0.013	0.017	0.005	0.009	0.023	0.011	0.006	0.007	0.016	nd	0.002	nd	0.002	0.006	nd
Er	0.070	0.034	0.035	0.013	0.014	0.015	0.040	0.048	0.017	0.025	0.065	0.031	0.015	0.017	0.036	0.001	0.006	nd	0.008	0.016	0.001
Tm	0.011	0.005	0.007	0.001	0.004	0.003	0.008	0.008	0.003	0.003	0.009	0.004	0.001	0.004	0.004	nd	0.002	nd	0.002	0.002	nd
Yb	0.059	0.029	0.030	0.009	0.013	0.017	0.038	0.047	0.016	0.020	0.056	0.027	0.010	0.014	0.022	nd	0.008	nd	0.010	0.013	0.001
Lu	0.018	0.007	0.012	nd	0.006	0.016	0.032	0.013	0.011	nd	0.014	0.007	nd	0.006	0.010	nd	0.007	nd	0.010	0.005	nd
Th	0.087	0.046	0.055	0.021	0.034	0.001	0.023	0.014	0.004	0.012	0.025	0.024	0.005	0.021	0.029	nd	nd	nd	nd	0.017	nd
U	0.067	0.032	0.022	0.008	0.009	0.039	0.019	0.039	0.051	0.021	0.033	0.011	0.010	0.009	0.016	0.033	0.039	0.030	0.044	0.013	0.027

TI, Thermally immature; TM, thermally mature; TPM, thermally post-mature and numbers represent time in hours; nd, below detection.

REE was 1.5 ppm. This amount decreased to 45 ppb after 48 h and then increased again to 2 ppm between 96 and 144 h and maintained an almost constant value up to the end of the experimental period. In the thermally post-mature sample, the sum of REE is much lower compared to the thermally immature and mature samples. After 24 h of reaction, the sum of REE in solution was only 2 ppb. This concentration increased to 58 ppb during168 h of reaction and decreased again to lower concentrations.

North American shale composite (NASC) normalized REE distribution patterns in weathering fluids are presented in Figs. 13.2–13.4. In the thermally immature samples, we observed a pattern that is significantly depleted in the LREE (La-Nd) and enriched in the MREE and HREE (Sm-Dy; Ho-Lu) with La/Sm ratios <1 and La/Yb ratio << 1. A similar pattern of LREE depletion, enrichment of the MREE and HREE was also observed in the weathering solutions of the thermally mature sample. In the thermally post-mature sample, we observed a slight depletion of the LREE, enrichment of the MREE and almost flat HREE pattern in the weathering solutions.

We calculated Ce/Ce* ratios of all weathering fluids collected over the entire experimental period (312 h). Ce/Ce* represents a cerium anomaly and was calculated using NASC-normalized values of Ce and adjacent
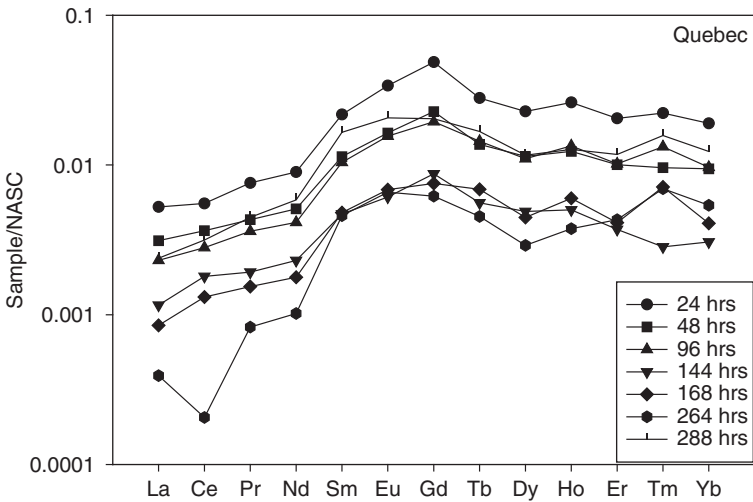

Figure 13.2.   Rare earth elements pattern in weathering fluids of thermally immature sample collected over 288-h reaction period. Concentration of REE in sample was normalized to the concentration of REE in North American shale composite (NASC) (Gromet et al., 1984).
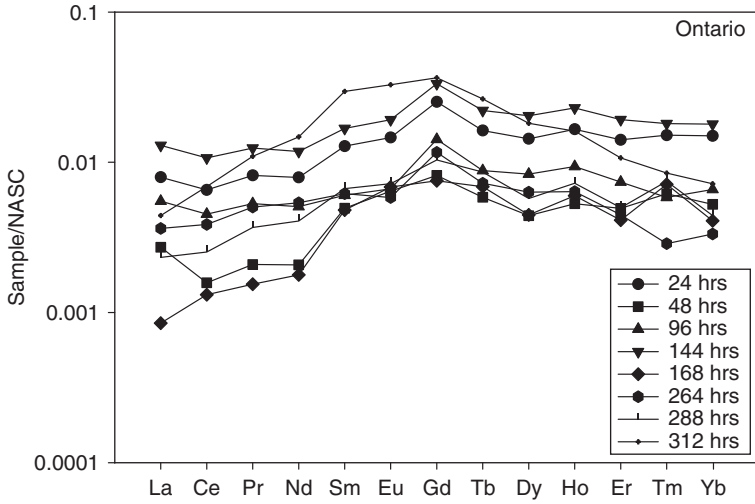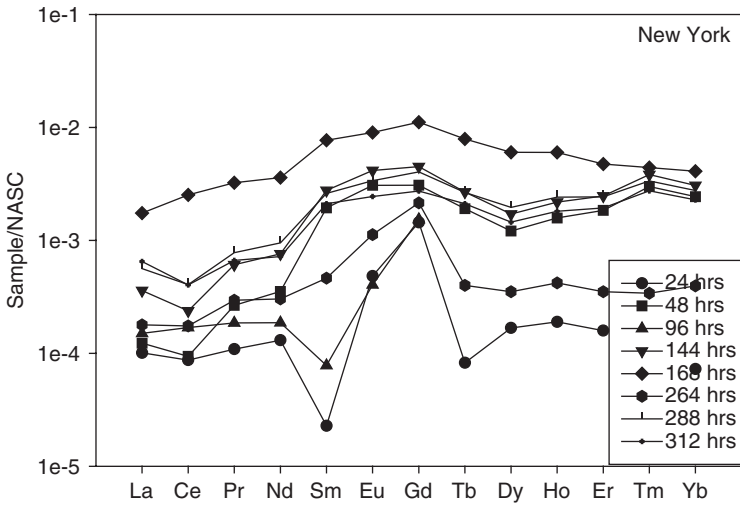
Figure 13.3. Rare earth elements pattern in weathering fluids of thermally mature sample collected over 312-h reaction period. Concentration of REE in sample was normalized to the concentration of REE in North American shale composite (NASC) (Gromet et al., 1984).

Figure 13.4. Rare earth elements pattern in weathering fluids of thermally post-mature sample collected over 288-h reaction period. Concentration of REE in sample was normalized to the concentration of REE in North American shale composite (NASC) (Gromet et al., 1984).

REE (La and Pr) (Taylor and McLennan, 1985). A majority of weathering fluids from the thermally immature shale sample show a slightly negative Ce anomaly (Ce/Ce* > 1). However, after 264 h of reaction time, a positive Ce anomaly of 1.29 was observed in the thermally immature sample. All weathering fluids from the mature sample collected over time result in a negative Ce anomaly with very little change over the entire experimental period. In the thermally post-mature sample, we observed variable Ce/Ce* with time as the experiment proceeded. Negative values were common during the beginning of the reaction up to 96 h of reaction time and slight positive values thereafter with punctuations of negative values.

13.4.3. Minor and trace elements

The concentrations of Ti, V, Cr, Ni, Zn, As, Sr, Ba, Th and U for all weathering fluids collected over time (24–312 h) are shown in Table 13.1. In the immature sample, the concentrations of several elements in solution tend to decrease with time with the highest concentrations occurring during the first 24 h of reaction. The rate of decrease in elemental concentration with time decreased steadily up to about 168 h of reaction time when the rate remains almost constant. However, certain elements, including Ti, Cr, Ni, As and U tend to increase in concentration after 168 h. In the thermally mature sample, a similar trend of decreasing elemental concentration with time was observed. With the exception of As, most trace elements in these samples maintained almost constant concentration after 168 h. Element release pattern in the post-mature sample was slightly different from that in the immature and mature samples. In the post-mature sample, the elemental concentration in the solutions collected over time stayed almost constant during the entire experimental period.

North American shale composite (NASC) normalized distribution pattern of Ti, V, Cr, Ni, Zn, As, Sr, Ba, Th and U for all samples are shown in Fig. 13.5–13.7. The following elements (Ca, Ti, V, Cr, Ni, Zn, As, Sr, Ba, Th and U) are all depleted in the weathering fluids relative to NASC. The degree of depletion is variable for different elements. Ti shows the highest degree of depletion in the immature and mature samples while Th shows the highest degree of depletion in the post-mature samples. Ti and V are almost equally depleted in the post-mature sample relative to NASC whereas in the mature and immature samples Ti is more depleted than V relative to NASC. However, the degree of depletion of Ti relative to V is higher in the immature sample compared to the mature sample. The concentration of As is close to that of NASC in all samples.
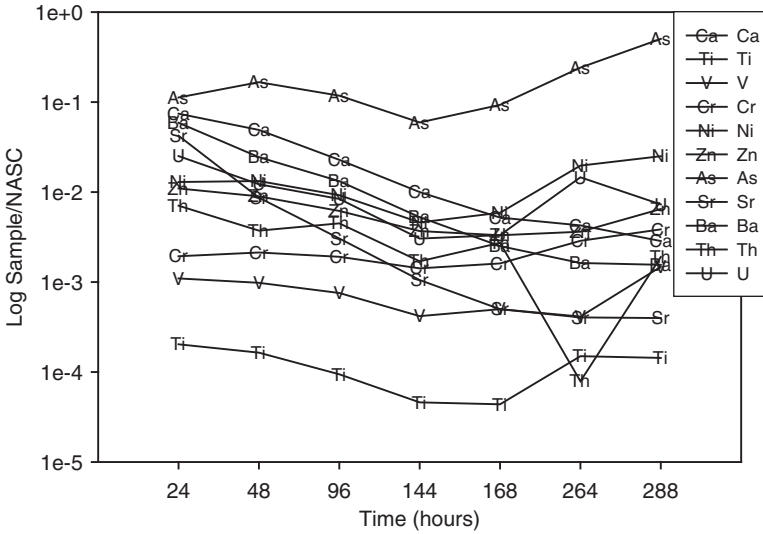
Figure 13.5. NASC normalized concentrations of minor and trace elements as a function of time in weathering fluids of thermally immature sample.
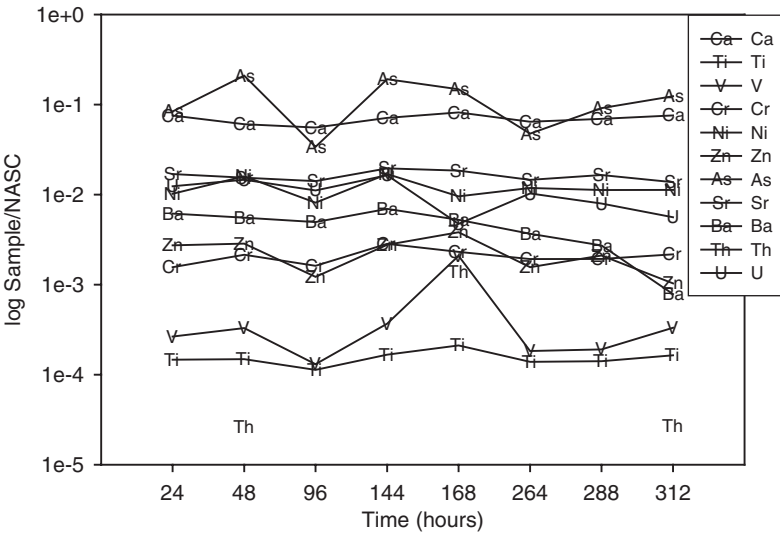

Figure 13.6. NASC normalized concentration of minor and trace elements as a function of time in weathering fluids of thermally mature sample.
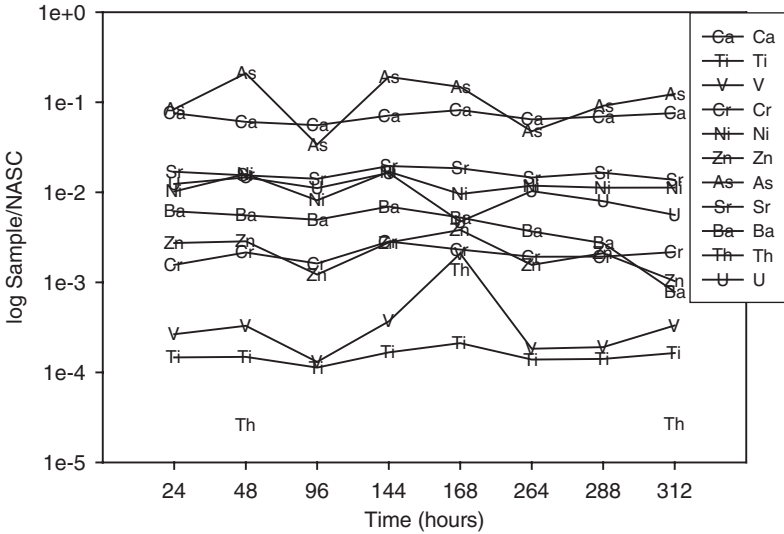
Figure 13.7. NASC normalized concentration of minor and trace elements as a function of time in weathering fluids of thermally post-mature sample.

We observed a general trend of decrease in elemental concentration with time for most of the elements analyzed. Since Ti is considered relatively immobile during chemical weathering (Ohmoto, 1996; Rye and Holland, 1998; White et al., 2001), we normalized the concentration of V, Cr, Ni, Zn, As, Sr, Ba, Th, U, La, Gd and Yb to the concentration of Ti in all weathering solutions and plotted these ratios on spider plots as shown in Fig. 13.8. When normalized to Ti, the ratio of all elements in the thermally immature sample excluding As, Ni and Cr decreased with time with a sharp decrease after 288 h. The ratio of As, Ni and Cr to Ti on the other hand increased with time over the entire experimental period. In the thermally mature samples, a similar trend of decreasing elemental concentration with time was observed with a sharp decrease during 48 h for the elements Th, U, La and Yb. In the thermally post-mature samples, the ratio of most elements to Ti remained almost constant over the entire reaction period.

13.5. Factor loadings

R-mode factor analysis was used to describe the relationship amongst dissolved constituents in the weathering fluids collected over a period of
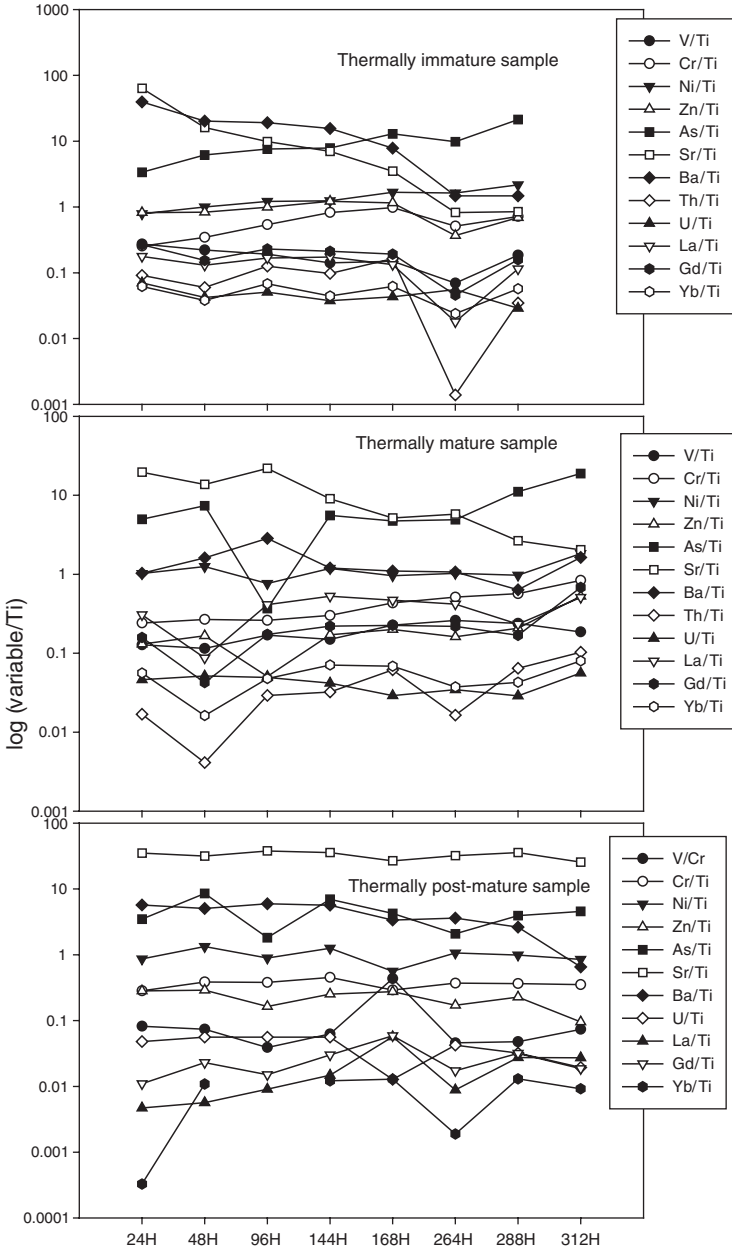
Figure 13.8. Minor and trace elements and selected REE concentrations in thermally immature, thermally mature and thermally post-mature samples normalized to concentration of Ti.

Table 13.2.   Factor loadings and communalities of variables in time dependent weathering solutions (Extraction method: principal components; rotation: varimax)

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Ti	0.048	−0.145	−0.464	0.846	0.140	0.947
V	0.106	−0.251	−0.254	0.088	0.907	0.968
Cr	−0.090	−0.113	−0.939	−0.005	0.245	0.963
Ni	0.082	−0.005	−0.929	0.325	−0.138	0.994
Zn	0.062	−0.883	−0.319	0.055	0.174	0.919
As	0.033	−0.021	−0.972	−0.067	0.137	0.969
Sr	0.035	0.620	0.060	0.711	0.114	0.907
Ba	0.148	−0.935	0.060	0.286	0.011	0.983
La	0.890	0.192	0.160	0.287	−0.118	0.952
Ce	0.970	0.079	0.173	0.095	0.028	0.986
Sm	0.831	−0.338	−0.180	−0.171	0.170	0.895
Eu	0.757	−0.544	−0.199	−0.100	0.142	0.938
Gd	0.854	−0.499	−0.011	0.070	0.057	0.987
Yb	0.810	−0.352	−0.195	0.270	−0.061	0.894
Th	0.398	−0.853	0.135	−0.071	0.133	0.927
U	0.185	−0.483	−0.362	0.618	−0.409	0.948
Percent of variance explained by factor						
	27.4	23.1	20	17.2	7.3	
Cumulative percent variance						
	27.4	50.5	70.5	87.7	95	

13 days of reaction time. Rotated factor loadings and communalities including the percent variance explained by each factor are shown in Table 13.2. The analysis resulted in five factors that we used in explaining the probable sources of Ti, V, Cr, Ni, Zn, As, Sr, Ba, Th, U and the REE (La, Ce, Sm, Eu, Gd and Yb) in the weathering solutions. These five factors explained about 95% of variance in our data. Factor 1 was the dominant factor and explained about 27.4% of the variance; factor 2 accounted for 23.1% of variance; factors 3 accounted for 20.0% of the variance while factors 4 and 5 accounted for 17.2% and 7.3% of the variance in our data, respectively. The remainder 5% could be attributable to noise.

Factor 1 (Fig. 13.9) had high loadings for La, Ce, Sm, Eu, Gd and Yb, intermediate loadings for Th and low loadings for Cr, Ba and U and almost zero loadings for Ti, V, Ni, Zn, As and Sr. Factor 2 (Fig. 13.10) had high loadings for V, Zn, Ba, Eu and Th, intermediate loadings for Sr, Sm, Gd and Yb, low loadings for Cr, Ni, La and U and almost zero loading for Ti, As and Ce. Factor 3 (Fig. 13.11) had high loadings for Cr, Ni and As, intermediate loadings for Ti, V and Zn, low loadings for Sr, Ba, La, Ce, Sm, Eu, Yb, Th and U and almost zero loading for Gd.
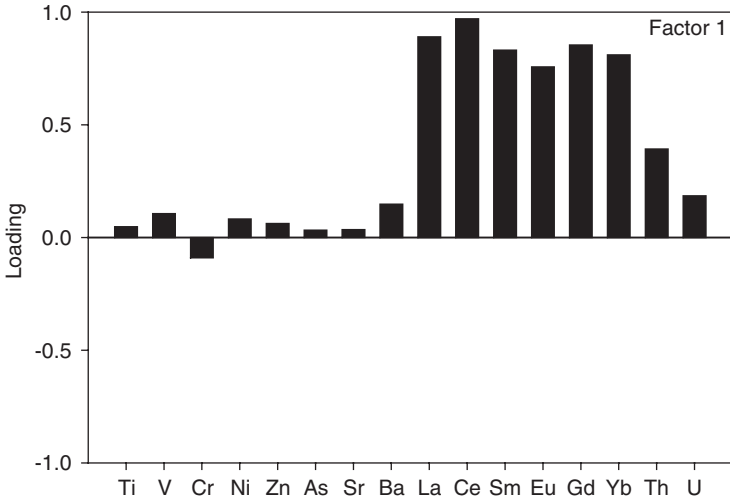
Figure 13.9.   Bar plot of rotated factor loadings (factor 1). This factor shows high loadings for the REE and intermediate to low loadings for Th and U.
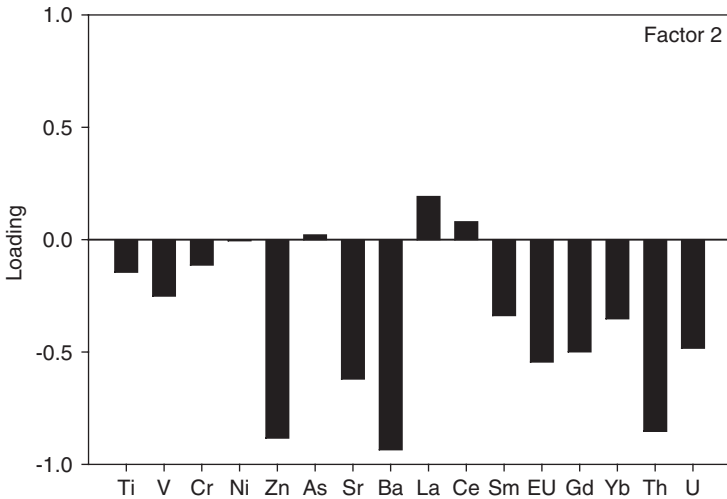

Figure 13.10.   Bar plot of rotated factor loadings (factor 2). Factor 3 shows high loadings for Zn, Sr, Ba and Th and intermediate to low loadings for Sm, Eu, Gd, Yb and U.
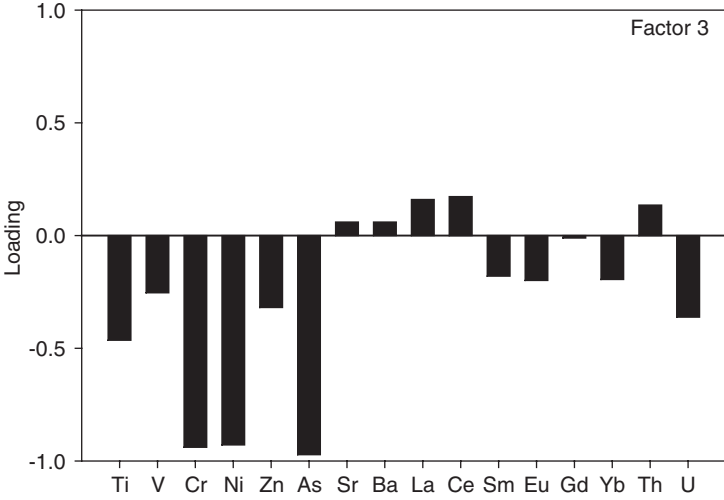
Figure 13.11. Bar plot of rotated factor loadings (factor 3). This factor shows high loadings for Cr, Ni and Zn and intermediate to low loading for Ti, V, Zn and U.
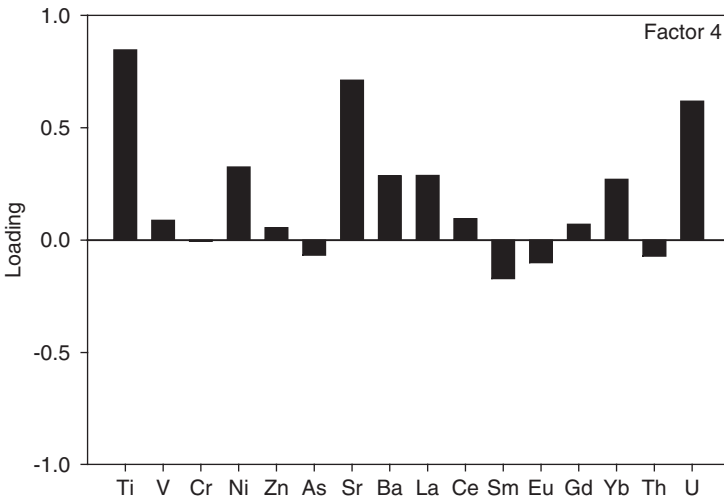

Figure 13.12. Bar plot of rotated factor loadings (factor 4). This factor shows high loadings for Ti, Sr and U and intermediate to low loading for Ni, Ba, La and Yb.
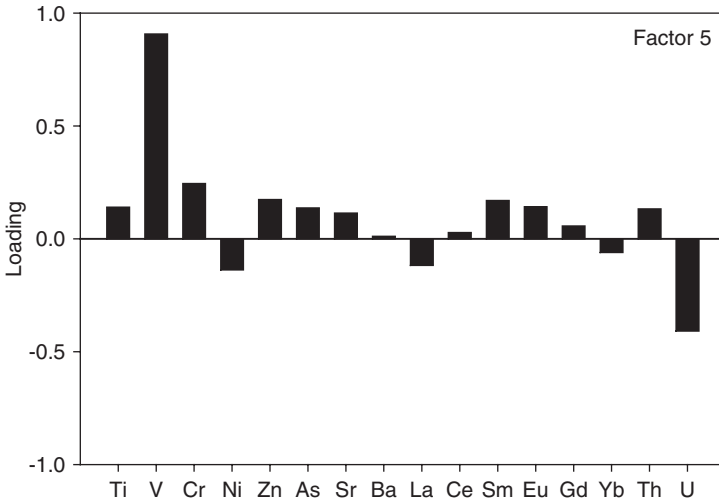
Figure 13.13. Bar plot of rotated factor loadings (factor 5). This factor shows high loading for V and intermediate for U.

Factor 4 (Fig. 13.12) had high loadings for Ti, Sr, Ba and U, intermediate loadings for Ni and Yb, low loadings for La, Sm and Th and almost zero loading for V, Cr, As, Ce and Eu. Factor V was essentially a Vanadium–Uranium factor, which had high loadings for V and low loadings for U and almost zero loading for all other variables (Fig. 13.13).

A second R-mode factor analysis was carried out using elements with known association to particular mineral phases in black shale. We selected La, Gd, Sr, Ni and V to represent elements associated with the clay, phosphate, carbonate and sulfide mineral phases, and organic matter, respectively (Patterson et al., 1986; Holly, 1990). Sorted rotated factor loadings and communalities for this analysis are presented in Table 13.2. This analysis resulted in four factors that explained over 96% of the variance in our data. In this analysis, we considered all variables with a factor score less than 0.3 as insignificant and gave those factors a zero value. Factor 1 had high loadings for La and Gd with zero loadings for V, Sr and Ni. Factor 2 had high loading for V, low loading for Gd and zero loading for Ni, La and Sr. Factor 3 had high loading for Sr and zero loading for V, Ni, La and Gd while factor 4 had high loading for Ni and zero loading for La, Gd, V, Sr and Ni.

To study whether these factors were related to each other, we performed a correlation analysis using the rotated factor scores (Fig. 13.14). The *r*-values were low in a majority of cases. The highest correlation
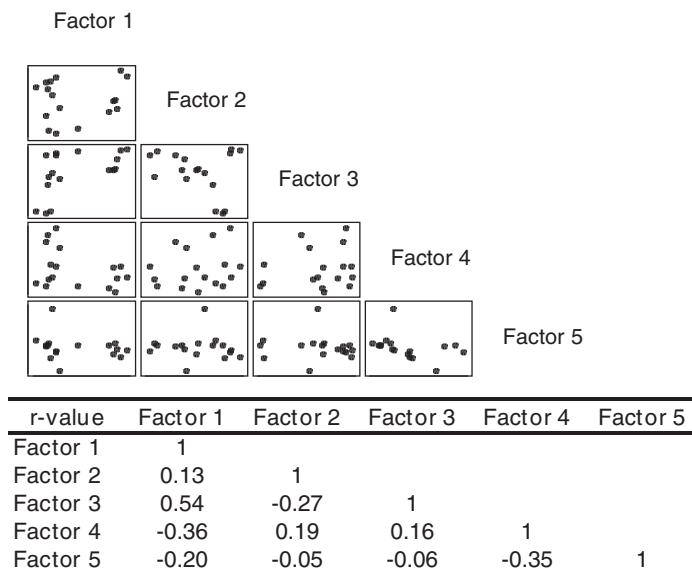
r-value	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Factor 1	1				
Factor 2	0.13	1			
Factor 3	0.54	-0.27	1		
Factor 4	-0.36	0.19	0.16	1	
Factor 5	-0.20	-0.05	-0.06	-0.35	1

Figure 13.14. Correlation matrix plots of rotated factor scores. The table shows *r*-values for correlations in the figure.

($r = 0.54$) was between factors 1 and 3. The absence of a significant correlation between these factors suggests that they were independent of each other.

13.6. Discussion

13.6.1. Interpretation of factor loadings

Statistical analysis (R-mode factor analysis) has been applied in many geochemical studies to determine the source of different elements or the association among dissolved constituents in aquatic media (Oloronfemi, 1984; Caggianelli et al., 1992; Vreča et al., 2001). The work of Reeder et al. (1972) provides a classic example in the use of R-mode factor analysis to explain the chemistry of natural waters resulting from the chemical weathering of bedrock. We applied R-mode statistical analysis to show the association between different elements in solution in order to identify their source. We also compared the patterns of REE in the weathering fluids to reported patterns of REE in major and easily weathered minerals associated with black shale (Taylor and McLennan, 1985; Kidder and

Table 13.3. Correlation matrix for minor and trace elements including selected REE

	Sr	Ba	Ti	V	Cr	Ni	Zn	As	La	Gd	Yb	Th	U
Sr	1												
Ba	**0.71**	1											
Ti	**0.65**	0.35	1										
V	0.08	0.28	0.27	1									
Cr	0.07	0.04	0.49	0.39	1								
Ni	0.15	0.06	**0.69**	0.16	**0.83**	1							
Zn	0.40	**0.83**	0.33	**0.52**	0.41	0.31	1						
As	−0.14	−0.06	0.37	0.44	**0.88**	**0.84**	0.35	1					
La	−0.10	0.08	0.10	0.16	−0.24	0.04	−0.02	−0.02	1				
Gd	0.17	**0.57**	0.11	0.43	0.00	0.09	**0.52**	0.16	**0.73**	1			
Yb	0.16	0.49	0.27	0.36	0.12	0.29	0.48	0.26	**0.80**	**0.88**	1		
Th	0.47	**0.83**	0.04	0.34	−0.03	−0.12	**0.79**	−0.11	0.21	**0.74**	**0.62**	1	
U	**0.67**	**0.60**	**0.72**	−0.10	0.28	0.61	0.44	0.22	0.13	0.29	0.40	0.32	1

Note: La, Gd and Yb$_{LA}$, Gd and Yb represent the light, middle and heavy REE, respectively.

Eddy-Dilek, 1994; Hannigan and Sholkovitz, 2001; Abanda and Hannigan, 2004). Description and interpretation of factor composition is discussed on the basis of breakdown of mineral phases associated with black shales. We interpreted factor 1 as representing the breakdown products of a REE-Th-U-rich mineral phase because of the high-loading scores of La, Ce, Sm, Eu, Gd and Yb, intermediate loadings of Th and low loading of U. Taylor and McLennan (1989) suggested that Th shows similar geochemical behavior to the REE while Burt (1989) suggested that the actinide U and Th commonly substitute for the REE in nature. The positive correlation between Th, U and the REE (Table 13.3) in our samples suggests control of these variables by a common factor. We submit that a REE-Th-U-rich mineral phase or a REE-rich mineral phase in which U and Th substitute for the REE may account for the observed high loadings of the REE and as a result the similar behavior of these elements during black shale weathering. Generally in sedimentary rocks, the REE occur in essential as well as accessory mineral constituents (Burt, 1989). REE distribution patterns in the weathering solutions result in a pattern that is enriched in the MREE and HREE and depleted in the LREE. Earlier studies have shown that the enrichment of MREE in black shales or in streams draining black shale catchments is related to the presence of phosphate minerals or to the weathering of phosphate minerals (Kidder and Eddy-Dilek, 1994; Hannigan and Sholkovitz, 2001). Since phosphate is one of the most easily weatherable minerals in black shales we think that factor 1 is controlled by the weathering of a REE–phosphate mineral phase. Possible minerals include monazite, xenotime

and apatite. High loadings of U associated with this factor may be due to weathering of a uranium-rich phase associated with phosphate. Uranium in the $+4$ and $+6$ states are the most common oxidation states in natural water systems. Uranium in the $+4$ oxidation state is essentially insoluble under oxidizing mildly acidic to alkaline conditions under which the leaching experiments were carried out. Conversely, U^{+6} ion is potentially much more mobile, because of the greater solubilities of most U^{+6} minerals (e.g., Osmond and Ivanovich, 1992). The above minerals have not been reported in the Utica shale samples, but it is likely that minor amounts of these minerals may exist that can account for the observed patterns of REE and U in our samples. It is also possible that desorption of REE bound to exchange sites on clay minerals may account for the observed high loadings of REE.

Factor 2 was interpreted as representing the weathering products of detrital clay mineral fraction. This factor had high loadings for Ba, Zn and Th that may be related to the breakdown of detrital material or source material from which the samples were derived. This may include weathering of clay minerals and plagioclase-feldspar, which may have contributed to high loadings of Eu thereby resulting in the observed positive Eu anomalies. We interpreted factor 3 as representing the weathering products (oxidation) of sulfide minerals as well as breakdown of detrital clay minerals because of the high loadings of Cr, Ni and As that are associated with sulfides (Patterson et al., 1986). This factor also had intermediate loading of Zn and Ti, elements that are usually associated with the detrital fraction. Since factor 1 was interpreted as the product of weathering of a REE-Th-U-rich phase and factor 3 as the product of breakdown of sulfide mineral phase as well as breakdown of detrital material, this may account for the slight positive correlation ($r = 0.52$) between factors 1 and 3 (Fig. 13.14). Factor 4 was interpreted as representing the breakdown products of carbonate and clay minerals due to the high loadings of Ti, Sr, Ba and U and intermediate loadings for Ni and Yb. Factor 5 was interpreted as representing the products of partial breakdown of organic matter because of the high loadings of Donald et al. (2000) showed that more vanadium is hosted by neomorphic illite than by organic matter in Pennsylvanian black shale from Indiana. It is possible that the high loadings of V associated with factor 5 may be the result of dissolution of illitic clays or the breakdown of organic matter associated with clay mineral surfaces (Kennedy et al., 2002). The leaching trends of V observed in this study, hint that V is more easily leached from the immature samples than the mature sample. In the post-mature sample, there is an abrupt increase in the concentration of V after 144 h of reaction but the concentration reduces significantly after 264 h. We submit that in the immature samples

V is associated more with organic matter while in the mature and post-mature samples V tends to associate with illite.

13.6.2. Identifying sources of trace element (mineral contribution) using R-mode factor analysis

R-mode factor analysis has been used in many geochemical studies to identify sources of metals (Reeder et al., 1972; Pattan et al., 1995). We used R-mode factor analysis to identify major controls of minor, trace and REE in solution from black shale weathering. Our results suggest that four major mineral phases including organic matter could be use to explain 95% of the observed elemental concentration in solution. A major REE mineral phase results in the release of high concentration of the REE in solution. Th and U are associated with this mineral phase, which suggests similar chemical behavior of these elements with the REE (Weimer et al., 1980). Weimer et al. (1980) have suggested the use of the REE as natural analogues for the actinides because of their similar chemical behavior. Sulfides, carbonates and detrital clay minerals also contribute substantially to the total dissolved load in the weathering fluids. Factor 5 that we ascribe to the weathering product of organic matter accounts for a small but reasonable portion of trace elements considering that the organic matter fraction in these shales is not readily oxidazable organic matter. Some research has shown that refractory organic matter occurs in soil profiles formed from weathering of Paleozoic black shale. It has also been reported that because of the refractory nature, this type of organic matter constitutes a sizable portion of total suspended solids in streams draining Paleozoic black shales basement (Petsch et al., 2000).

13.6.3. REE fractionation patterns in weathering solutions

REE fractionation during weathering of parent material has been reported by Nesbitt (1979). The patterns of REE in minerals associated with black shales have been reported in a number of studies (Taylor and McLennan, 1985; Kidder and Eddy-Dilek, 1994; Hannigan and Sholkovitz, 2001). Taylor and McLennan, (1985) in their review of the upper continental crust and its composition, reported the patterns of REE in common rock forming minerals as well as in common accessory minerals in sedimentary rocks. In black shales trace elements and the REE are associated with a number of phases including ion exchange sites on clay minerals, adsorbed on ferric oxides and aluminum oxides, adsorbed to organic matter, co-precipitated as carbonate and bound to crystalline mineral phases. Accessory (heavy minerals) associated with

black shale also carry a significant amount of trace elements and the REE especially the HREE (Taylor and McLennan, 1985). As Taylor and McLennan (1985) suggested, an understanding of REE chemistry during black shale weathering will allow for greater understanding of the weathering process in these rocks. Proper understanding of trace element and REE mobility during weathering of black shale would allow for elimination of misinterpretation of sedimentary REE patterns and consequently interpretation of source material.

With increasing reaction time accompanied by decreasing concentration of REE in the weathering solutions we observed a decrease in the $(La/Sm)_N$ ratio from about 0.25 to 0.10 in the thermally immature sample. The thermally mature and thermally post-mature samples also show similar decrease in $(La/Sm)_N$ ratio with decreasing REE concentration and increasing reaction time. However, the average $(La/Sm)_N$ ratio is higher in the thermally mature sample compared to the thermally immature and thermally post-mature samples (thermally mature > thermally post-mature > thermally immature). This result suggests that the enrichment of the MREE is higher in the thermally mature sample relative to the thermally post-mature and thermally immature samples. Weathering of the Utica shales therefore results in the fractionation of REE leading to enrichment of MREE in solution as shown in Figs. 13.2–13.4 and as reported by other workers (Braun et al., 1998; Zhang et al., 1998; Leleyter et al., 1999; Aubert et al., 2001; Hannigan and Sholkovitz, 2001; Gnandi and Tobschall, 2003; Ji et al., 2004). It is likely that this fractionation is the result of different weathering rates of host mineral phases in rock and not related to source signature since the pattern of REE in the whole rock is different. In the whole rock the pattern of REE shows enrichment in the LREE and depleted in the MREE and HREE (Abanda, 2005). Earlier research has shown that the MREE are associated with phosphate mineral phase in black shale (Hannigan and Sholkovitz, 2001; Kidder et al., 2003). The breakdown of this phase during weathering may lead to preferential release of the MREE relative to the LREE as shown by enrichment of the MREE in our samples (La/Sm < 1).

We calculated the partition coefficients between the solid and liquid phases for all elements analyzed in this study using the concentration of the elements in the weathering solutions and their corresponding concentrations in the whole rock samples. Ideally, partition coefficients are computed for solutions in equilibrium with pure mineral phases. In our case, we cannot infer equilibrium and also multiple mineral phases were involved. In general, $\log K_d$ for most elements was highest at the beginning of the reaction but decreased slowly over time. For the following elements As, Ba, Sr, Zn, Ni, Cr, U, V, La, Gd and Yb, $\log K_d$ ranged

between -0.7 and -3.5. $\log K_d$ for these elements follows the order $As > Ba > Sr > ZnYbNi > GdLa > Cr > U > V$. The observed high $\log K_d$ for As may be related to rapid breakdown of sulfide minerals. Ba and Sr are relatively more mobile during chemical weathering (Picouet et al., 2002; Singh et al., 2005), which may account for the high $\log K_d$ values of these elements. On the other hand, the REE and Cr are considered relatively immobile during chemical weathering (Taylor and McLennan, 1985) thereby lending support to the low $\log K_d$ values for these elements. Our results suggest that the Gd (MREE) and Yb (HREE) are relatively more mobile than La (LREE) during weathering of the Utica shales leading to higher $\log K_d$ for Gd and Yb (-2.3 and -2.0, respectively) relative to La (-2.6). $\log K_d$ for Sr decreased significantly from -1.1 after 24 h to -3.2 after 288 h of reaction. This result corroborates the association of Sr with the carbonate phase because we expect rapid dissolution of carbonate mineral at the beginning of the experiment. We suggested that V is associated with the organic fraction and it is not surprising that the $\log K_d$ for V is exceptionally low (~ -3.5). Petsch et al. (2000) reported that refractory organic matter in Palaeozoic black shale is not very susceptible to chemical weathering and may therefore hold onto trace elements associated with this fraction.

13.7. Conclusions

The study of chemical weathering of black shales is important because of the abundance of these rocks in the sedimentary record and their role in controlling the composition of chemical species in associated natural water systems and consequently on water quality. Although much experimental work has been done on the weathering of pure minerals as well as weathering of rocks in which the modal mineralogy can easily be estimated, little experimental work has been done on studying the weathering of a fine-grained multimineralic rock rich in organic matter. This research reports the results of the application of multivariate statistical analysis (R-mode factor analysis) in assessing geochemical data from experimental study of black shale weathering thus allowing the identification of different mineral phases contributions to the composition of chemical species (minor trace and REE) in solution. R-mode factor analysis suggests that four major mineral phases (phosphates, carbonates, silicates and sulfides) including organic matter are important in controlling trace elements and the REE in solution from the weathering of black shale. Laboratory weathering of black shale results in elevated concentrations of minor and trace elements including the REE in weathering solutions relative to the concentrations

of these elements in natural water systems. Extension of results from experimental studies of black shale weathering to model natural weathering of black shale in the field will necessitate detail mineralogical study of the rocks and mass balance calculations to determine the contribution of individual mineral phases and organic matter to the total elemental composition of chemical species in solution. We also showed that weathering of the black shale leads to significant fractionation of the REE with the MREE and the HREE being more mobile than the LREE. Slight differences occur between the weathering patterns of rocks of different thermal grades, which can be ascribed to diagenetic modifications. We observed that in the thermally post-mature sample the LREE are slightly depleted in the weathering solutions relative to the thermally mature and thermally immature samples.

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