

Influence of Mineralogy and Geological Setting on Trace Metal Concentration within Subtropical Weathered Profiles, Bells Creek Catchment, Queensland, Australia¹

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Abstract: The effects of mineralogy and geological setting on trace metal concentration and distribution within six weathered profiles developed sandstone and mudstone was assessed. Primary minerals occurring in the weathered profiles are quartz, plagioclase, and K-feldspar. Kaolinite is the most dominant secondary mineral followed by mixed layers of smectite-illite, illite, hematite, siderite, and occasional calcite. Metal concentrations within fresh and weathered samples were investigated by two methods of digestions: HF-based digestion and aqua regia. Results revealed that V and Cr are largely present in the primary aluminosilicate matrix and are not easily available to the environment; however, Cu, Zn, and Pb are present in extractable forms and readily leached. Iron occurs in both primary minerals and insoluble secondary minerals such as hematite. The mineralogical study also showed that drill hole material with more clay minerals tends to contain higher metal concentrations, demonstrating that mineral composition is the major control over trace metal content. Spearman's rank correlation matrix also confirmed the role of mineralogy on trace metal concentration (e.g., V and Cr correlated with kaolinite and Pb correlated well with mixed layers of illite-smectite). Effect of geological setting on trace metal concentration was assessed by examining the geomorphological location of drill holes with respect to paleochannels, surface topography, and water table position. Results revealed that depth of burial of the weathered profile does not have an important effect on weathering and trace metal composition of samples. However, samples located on flat terrain and with shallow water table are more prone to leach metals. Factors controlling degree of chemical weathering and subsequent trace metal distribution are summarized in order of importance: mineralogy > geological setting (topography and parent rock type) > water table depth > depth of profile burial.

CHEMICAL WEATHERING of rocks is one of the major processes that modify the earth's surface and is one of the key processes contri-

buting to the geochemical cycling of elements (Berner and Berner 1996). The effect of geological setting (e.g., parent rock type and topography), climate, and position of water table on chemical weathering of rocks is well documented (e.g., Jenny 1941, Loughnan 1969, Summerfield 1991, Macias and Chesworth 1992, Thomas 1994, Hill et al. 2000, Taylor and Eggleton 2001). For example, the subtropical climate of southeastern Queensland is a paramount factor in chemical weathering throughout the study area, as it readily produced highly weathered profiles such as those beneath the Tertiary land surfaces, which have undergone deeper weathering and induration than the interfluves (Grimes et al. 1986). In addition, by controlling weathering

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processes, topography can also influence the trace metal composition of both weathered bedrock and the underlying layers (Boggs 1995).

The mobilization and redistribution of trace metals during weathering are substantially affected by various processes such as dissolution of primary minerals and formation of secondary phases. Other factors that are important are pH and Eh conditions (e.g., Harris and Adams 1966, Chesworth et al. 1981, Cramer and Nesbitt 1983), soil texture (Richards et al. 2000), biological activities (Welch and McPhail 2003), and amount of organic matter (Kaschl et al. 2002, Udom et al. 2004). During weathering of crystalline rocks, primary mineral phases are partly dissolved, and hydrolysis and hydration take place. Secondary minerals such as illite and smectite are commonly the earliest to be formed, followed by halloysite and kaolinite. In the final stage, as leaching intensifies, partial desilicification occurs and kaolinite is converted to gibbsite. Feldspars, for example, often weather directly to an amorphous phase (Fields and Swindale 1954), then to kaolinite (McCaleb 1959, Exley 1976), and ultimately to gibbsite or boehmite (Helgeson et al. 1969, Parham 1969, Lodding 1972).

Reported studies investigating the roles of mineralogy, topography, and parent material on the trace metal concentration in sedimentary weathered profiles are limited due to either the lesser abundance of these rocks (only 5% of earth crust [Carroll 1970]) or their limited economic value. The aim of this study was therefore to investigate the extent to which mineral composition, topography, and parent material control trace metal distribution within sedimentary weathered profiles occurring in a subtropical setting. This investigation also increased our understanding of weathering mechanisms and trace metal distribution/mobility. In addition, although some of the profiles are present near the land surface, others are buried under thick layers of young unconsolidated sediments; the effect of this aspect of the setting on weathering and trace metal contents of the samples was therefore investigated. Stratigraphic and hydrogeological drilling in Bells

Creek catchment, southeastern Queensland (Figure 1) provided the opportunity to investigate several types of buried and exposed weathered profiles.

Digestion methods such as HF-based total digestion and aqua regia (partial digestion) are used to determine the amount of heavy metals potentially available in total rock in comparison with the same metals present in extractable forms. Such comparisons can be of importance to the environmental assessment of areas under development pressure, because studies of trace metals in soil typically represent bulk concentrations rather than comparisons between total and extractable metal concentrations.

Study Area

GEOMORPHIC FEATURES OF THE STUDY AREA. The Bells Creek catchment is predominately low lying (typically with relief of <10 m) and covers an area of 100 km². It is located about 80 km north of Brisbane and is within the northern section of the Pumicestone region (Figure 1). The maximum elevation of the coastal plain in this catchment is around 55 m above sea level in the bedrock hills to the west; the central alluvial plain is less than 20 m, and in the eastern strip the elevation is less than 5 m (Department of Natural Resources and Mines, unpubl. data).

Climatically, Bells Creek catchment is typical of southeast Queensland, which is subtropical with hot, wet summers and mild, dry winters. Mean rainfall over the 5-yr period (1998–2003) varies from 1,340 mm/yr in the south of the catchment to 1,580 mm/yr in the north. Mean daily temperatures range from 15 to 30°C in summer and 9 to 20°C in winter. Within the region there is a wide range of land-use practices including pine plantation, sugarcane, and horticulture; *Melaleuca* bush land is common along drainage lines, and mangrove forests are well developed along catchments and estuaries. The current land use in the catchment is predominantly pine plantation.

GEOLOGICAL SETTING. The Pumicestone region is part of an intracratonic basin, which accommodated a large fluvial system during

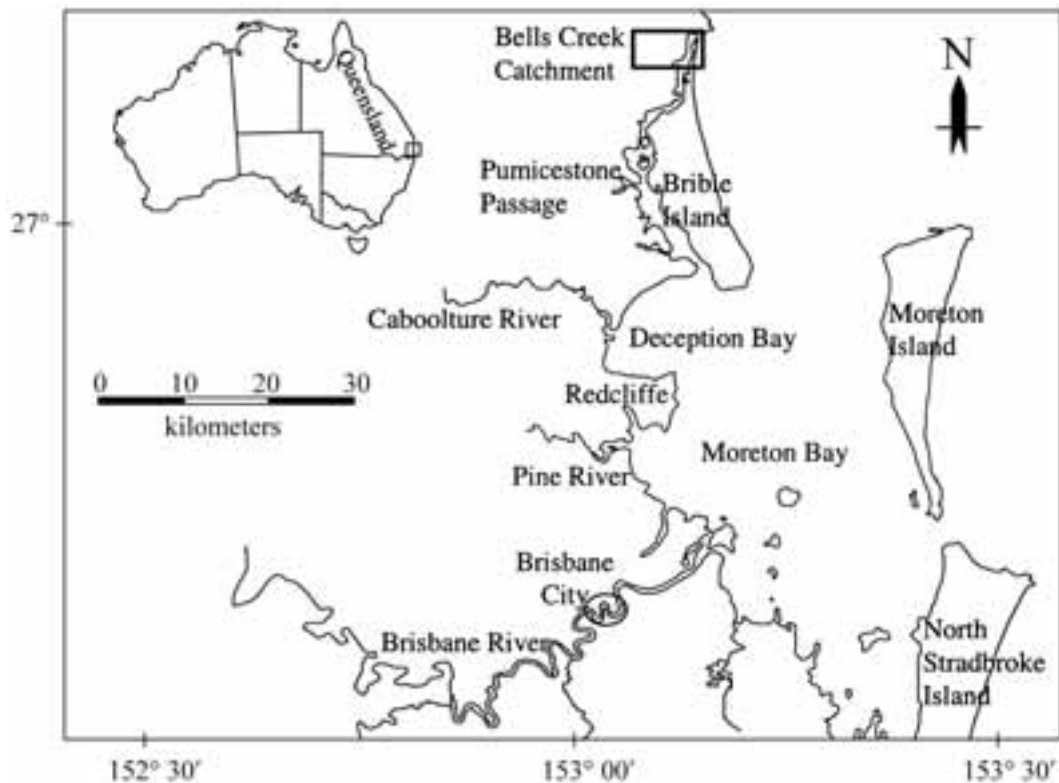


FIGURE 1. Location of the study area (rectangle at top of map) in relation to Pumicestone region and Moreton Bay in southeastern Queensland.

the early to middle Mesozoic (Cranfield 1983, Murphy et al. 1987). A variety of pre-existing, largely volcanic rocks have been eroded and supplied the fluvial system with material that was eventually incorporated in the Landsborough Sandstone, which is the only rock exposed in the catchment. This formation, which today represents the bedrock of the region, consists of quartzo-feldspathic sandstone with lithic fragments of volcanic origin and layers of shale, conglomerate, mudstone, and coal (e.g., Murphy et al. 1987). The sandstone consists mainly of quartz, plagioclase, occasional muscovite, and variable amounts of minerals of volcanic origin (mafic and titaniferous minerals, and glass) (Hawkins 1983). The most abundant weathering products are kaolinite and hematite (Preda and Cox 2002, Ezzy et al. 2003).

During low sea level conditions of the

Pleistocene period (~2 Ma), the eastern Australian continental shelf was exposed and incised by river systems. Subsequent rise in sea level led to the drowning of river channels and development of estuaries and coastal plains. In southeast Queensland, the current interglacial high stand was reached about 6,500 yr ago (Williams et al. 1998) when sea level was approximately 1.0 m higher than the present day; after 3,000 years B.P. the sea level in the Pumicestone region appears to have fallen to its current position (Flood 1981, Lester et al. 2000).

The heterogeneous character of the bedrock formation and the lability of the sandstone have led to the development of thick weathering profiles clearly due to exposure since the Pleistocene (Ezzy et al. 2002). The Bells Creek catchment is situated on the narrow coastal floodplain on Quaternary-age

sedimentary material and outcropping Landsborough Sandstone bedrock. During low sea level episodes, down cutting into the bedrock led to the development of depressions and channels that eventually infilled with sediments during stages of higher sea level (Ezzy and Cox 2003). Recent investigations using ground-penetrating radar enabled the identification and visualization of the deeper coastal sequences and their depositional environment. Ezzy et al. (2003) investigated over 30 north-south and east-west ground-penetrating radar profiles revealing that the sand-rich alluvial channels are typically 5 to 8 m thick, with widths of between 50 and 200 m. In areas where coarse-grained paleochannel sand horizons occurred in the

upper weathered bedrock horizon, penetration was up to 5 m and bedding characteristics and channel morphologies could be interpreted. The associated drilling program confirmed the complex sedimentary architecture of the area and also enabled sampling of a number of buried weathered bedrock profiles.

MATERIALS AND METHODS

Sampling Strategy

The samples analyzed in this study were obtained by rotary drilling and consist of weathered and fresh parent material (Table 1, Figure 2). Drill cores were subsampled,

TABLE 1
Sample Locations: Depth and Characteristics

Sample	Depth (m)	Core Characteristics ^a
S1-1	2-3	No alluvial cover, water table just below surface
S1-2	4-5	0-13 m weathered bedrock
S1-3	8-9	>13 m fresh mudstone
S1-4	12-13	Nonchannel drill hole
S1-5	13-15	
B3-1	14	0-14 m fluvial channel sands
B3-2	16	14-20 m weathered material
B3-3	18	>20 m fresh sandstone
B3-4	20	Channel drill hole
B7-1	8-8.5	0-7 m fluvial channel sands and shallow water table
B7-2	8.5-9	7-9.5 m weathered bedrock
B7-3	9-9.5	>9.5 m fresh sandstone
B7-4	9.5-10	Channel drill hole
L1-1	6	0-6 m clay-rich alluvium, water table 1 m below surface
L1-2	9	6-16 m weathered bedrock
L1-3	12	>16 m fresh mudstone
L1-4	14	Nonchannel drill hole
L1-5	16.4	
GB1-1	16.5	0-16.5 m coastal sand, water table ~3 m
GB1-2	18	16.5-25.5 m weathered rock
GB1-3	20	>25.5 m fresh mudstone
GB1-4	22	Channel drill hole
GB1-5	26	
H5-1	3-4	0-3 m fine-grained clayey sand
H5-2	4-5	3-13 m weathered bedrock
H5-3	5-6	>13 m fresh mudstone
H5-4	8-9	Channel drill hole
H5-5	10-11	
H5-6	12-13	
H5-7	13-14	

^a Data taken from T. R. Ezzy, M.E.C., J. O'Rourke, and G. J. Huftile, unpubl. data.

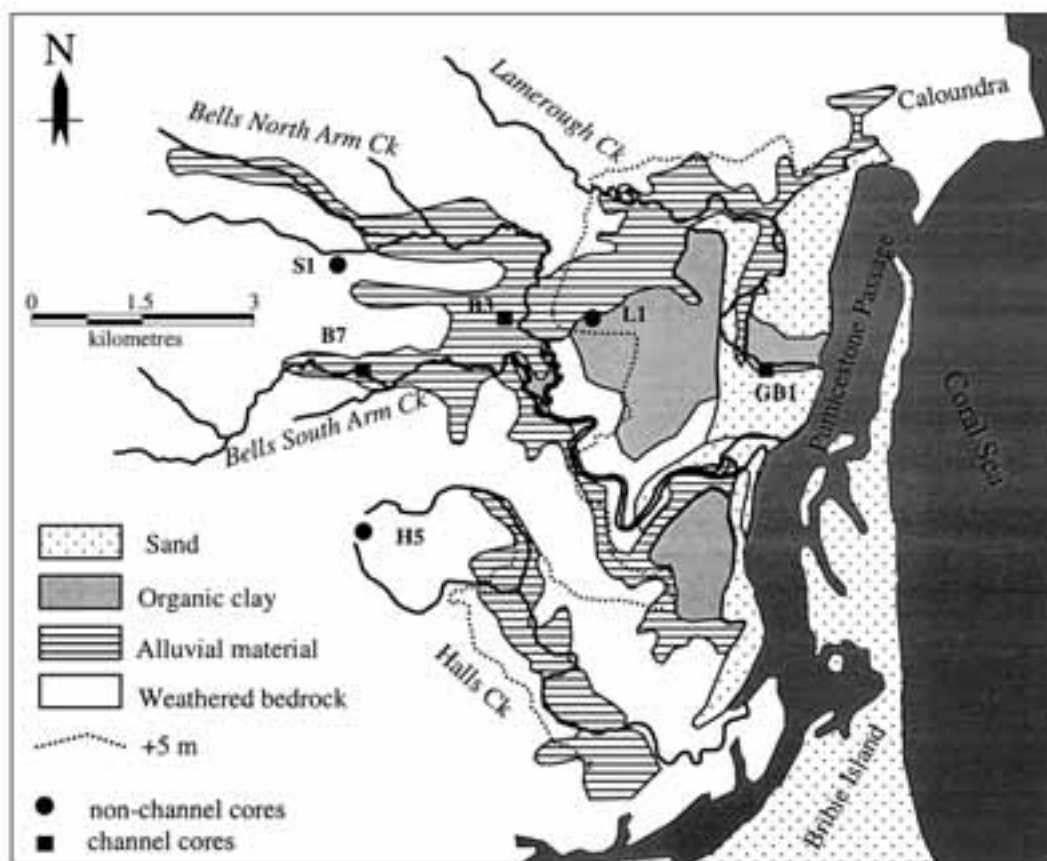


FIGURE 2. Core locations with respect to surficial material (after NSR Environmental Consultants 1999).

dried at 80°C for 24 hr, and comminuted with porcelain mortar and pestle. The drill holes are located on the main sedimentary rocks of the area (sandstone and mudstone) and also provided evidence on the role of the setting on weathering. Based on a concurrent study (T. R. Ezzy, M.E.C., J. O'Rourke, and G. J. Huftile, unpubl. data) of the stratigraphy of the area, it was confirmed that the material analyzed here has been weathered in situ and is not transported.

Drill holes studied here (T. R. Ezzy, M.E.C., J. O'Rourke, and G. J. Huftile, unpubl. data) can be categorized as being within (a) channel materials on top of Mesozoic sandstone (B3 and B7), (b) channel materials on top of Mesozoic mudstone (GB1), and (c) into thin (~2–3 m) alluvium on top of Meso-

zoic mudstone (S1, L1, and H5). These drill holes are shown in Figure 2.

Analytical Methods

To measure cations adsorbed by clays, organic matter, carbonates, and oxides, the samples were digested in concentrated aqua regia (1 HNO₃: 3 HCl) following a procedure recommended by the International Organization for Standardization (ISO 1995). Samples were oven dried overnight at 100°C and 1 g was mixed with 1 ml HNO₃ and 3 ml HCl and digested in a water bath at 95°C for 4 hr. The digests were quantified using an inductively coupled plasma optional emission spectrometer (ICP-OES) (Varian Liberty 200). The trace and minor metals analyzed

were V, Cr, Co, Ni, Cu, Zn, Pb, Fe, Mn, and Al.

To determine the total trace metal content (V, Cr, Co, Ni, Cu, Zn, and Pb), 100 mg of total sample was digested by 2.5 ml of HF and 5 mL of HNO₃ following a procedure described in Eggins et al. (1997). Samples were analyzed on an inductively coupled plasma mass spectrometer (ICP-MS) (Fisons PQ2+ Plasmaquad). This method was used also to determine concentrations of trace elements contained in silicate structures as a comparison with those that are more easily extractable and readily available to the environment.

The mineral composition of weathered and fresh bedrock was determined using X-ray diffraction and a diffractometer (Philips PW 1050) equipped with a cobalt anode. Nonoriented powder samples were used to obtain total composition; oriented specimens were prepared for clay identification. The quantification of mineral phases was assisted by SIROQUANT (quantification program that expresses the composition of crystalline material within a sample in percentage of dry weight), which provides quantitative analyses of mineral phases based on the principle of Rietveld analysis (pattern synthesis). An ideal X-ray diffraction pattern is synthesized from basic crystal structure data for each mineral in the sample. These synthesized patterns are added and fitted by a least squares refinement to the sample pattern. The quantification of the experimental X-ray diffraction trace is thus indirectly performed by quantifying the synthesized pattern. There is rarely a perfect fit between a calculated (synthesized) pattern and the observed (experimental) one; this imperfect fit results in errors in the quantification of each mineral phase. For the current investigation, an approximate phase error of 1% is common to most mineral phases identified. The errors are mainly based on the goodness of fit between the synthesized X-ray diffraction pattern and the experimental one. Larger errors were recorded for phases present in quantities larger than 30%. Errors of up to 3% have been reported for Rietveld analysis of similar estuarine sediments (Preda and Cox 2004) and artificial mixes of sandstones (Hillier 2000).

Statistical Analysis

Correlation indices were calculated to determine the relationship between metal concentrations and potential inorganic scavengers (e.g., clay minerals, Fe and Mn oxides) that influence metal mobility and distribution within weathered material. Geochemical data such as produced in this study are not normally distributed, so Spearman's rank correlation was used because this method is more appropriate than a simple linear correlation (e.g., Pearson). Spearman's correlation matrix was generated using the statistical package SPSS v.10.

Quality Control Procedures

The precision and recovery level of the analytical procedure for acid digestion (aqua regia) and metal determination by ICP-OES were tested using the marine sediment reference standard PACS-2 (National Research Council Canada). This is a certified reference material (CRM) for total digestion, because CRM was not available for extractable method using aqua regia. Recoveries of most metals from the reference material were >60%, except for V, Cr, Al, and Mn (Table 2). Vanadium and Cr are refractory metals, which strongly adsorb to siliceous materials; aluminum is part of the aluminosilicate matrix and the aqua regia digestion method is not robust enough to extract these metals. A low recovery percentage for Cr and Al had also been recorded by previous workers using a similar digestion method (Cook et al. 1997, Tam and Yao 1998). Means and standard deviations of the replicate samples were calculated. A comparison between the standard deviation of certified samples and replicate samples in this study revealed that repeatability generally had a relative standard deviation of <5% even when recoveries were low (Table 2).

For quality assessment of the HF-based digestion, the standard BHVO-1 was analyzed. The results are shown in Table 3 along with relative standard deviation obtained for this standard in the Advanced Centre for Queensland University Isotope Research Excellence

TABLE 2
Evaluation of Analytical Procedure Using Aqua Regia Digestion

Element	Certified ^a (mg/kg)	Found ^b (mg/kg)	Recovery (%)	Precision (% RSD) ^c
V	133 ± 5	62 ± 1.7	46.6	3
Cr	90.7 ± 4.6	42 ± 1.2	46.3	3
Mo	5.43 ± 0.28	3.4 ± 0.4	62	12
Co	11.5 ± 0.3	8.2 ± 0.3	71	4
Ni	39.5 ± 2.3	25 ± 0.7	63	2
Cu	310 ± 12	289 ± 6	93	2
Zn	364 ± 23	346 ± 8	95	2
Pb	183 ± 8	166 ± 7	91	4
As	26.2 ± 1.5	21 ± 0.5	80	2
Fe	40,900 ± 6,000	27,628 ± 828	68	3
Mn	440 ± 19	208 ± 6	47.3	3
Al	66,200 ± 3,200	13,385 ± 534	20	4

^a Certified Standard Reference Material, PACS-2 (harbor sediment, Canada).

^b Mean and standard deviation of three replicated extractions are shown.

^c RSD, relative standard deviation.

(ACQUIRE) laboratory. Both recovery level and precision were high, showing values of 94–100% and <6%, respectively.

RESULTS

Trace and Minor Element Occurrence

Based on concentrations of extractable cations the dominant trace metals measured are Zn, V, and Cr, followed by Cu and Pb (Table 4). Elements such as Co and Ni generally occur below detection limit, except in core GB1, which has the highest metal content

TABLE 3

Evaluation of Analytical Procedure Using HF Digestion

Element	Certified ^a (mg/kg)	Found ^b (mg/kg)	Recovery (%)	Precision (% RSD)
V	317	305	96	1.4
Cr	289	291	100	2.7
Co	45	44.2	97	1.4
Ni	121	114	94	3.9
Cu	136	131	96	5.8
Zn	105	103	98	5.4
Pb	—	1.95	—	3.8
Fe	85,541	84,291	98	—
Mn	1,301	1,290	99	—

^a Recommended values for basalt standard, BHVO-1, from Govindaraju (1994).

^b Results found by ACQUIRE laboratory.

for all the trace and minor elements. Trace elements such as Co, Ni, Cu, and Zn are more abundant in fresh rock than its weathered counterparts, suggesting that they are being depleted by leaching (Liaghati, Preda and Cox, unpubl. data). Metals such as V and Cr occur in higher concentrations in the weathered materials probably due to their immobility and consequent accumulation. Concentration of iron in fresh rock ranges from 11,000 to 28,000 mg/kg, but iron concentration fluctuates more in its weathered counterpart (300 to 119,000 mg/kg) (Table 4). Minor elements such as Al and Mn behave in a different manner than Fe. Although Al occurs in similar concentrations in both fresh and weathered material, Mn concentration is substantially higher in fresh parent rock compared with the weathered layer. For example, in core S1, manganese concentration in fresh rock is 23 times greater than average concentration in its weathered counterpart (Table 4).

Total versus Extractable Metal

To clarify controls over trace metal behavior within weathered profiles, a comparison between total metal composition and the readily available extractable component was conducted (Table 5). Such a comparison also

TABLE 4
Extractable Trace Element Contents (mg/kg) Determined by Aqua Regia for Selected Weathered Profiles

Sample	V	Cr	Co	Ni	Cu	Zn	Pb	Fe	Mn	Al
S1-1	14	3	<1.2	<1.5	1	54	<3	1,169	17	3,930
S1-2	41	15	<1.2	<1.5	1	53	7	36,149	3	8,214
S1-3	13	5	3	4	8	67	9	27,048	20	7,946
S1-4	3	1	2	2	3	31	4	2,146	5	1,028
S1-5	9	4	15	10	14	137	15	17,882	262	2,823
B3-1	9	3	9	5	5	126	9	13,014	620	1,488
B3-2	9	3	11	7	3	51	5	23,680	620	1,003
B3-3	12	5	9	4	3	67	7	12,119	755	1,481
B3-4	20	7	10	6	4	64	7	26,411	1,300	1,834
L1-1	3	4	<1.2	<1.5	1	21	4	488	3	4,954
L1-2	3	2	<1.2	<1.5	1	26	<3	294	3	2,834
L1-3	5	2	<1.2	<1.5	1	50	<3	2,262	19	2,549
L1-4	10	3	1.2	<1.5	2	37	5	15,887	28	3,583
L1-5	12	5	14	9	8	105	15	28,330	819	5,098
GB1-1	4	5	<1.2	2	1	61	<3	822	8	2,312
GB1-2	284	352	10	63	55	77	6	38,226	50	11,118
GB1-3	201	475	24	116	54	95	4	119,736	65	16,461
GB1-4	70	54	59	200	89	100	<3	14,893	35	10,773
GB1-5	9	27	19	46	10	111	7	15,694	69	7,669
H5-1	34	10	<1.2	<1.5	<0.5	43	6	22,285	5	10,863
H5-2	28	7	<1.2	<1.5	<0.5	37	12	15,498	2	7,981
H5-3	36	8	<1.2	<1.5	0.84	26	14	23,157	4	9,557
H5-4	28	5	<1.2	<1.5	2	47	6	30,741	18	5,579
H5-5	19	6	<1.2	1.5	3	56	8	23,208	57	10,526
H5-6	30	7	<1.2	1.5	5	138	32	29,802	40	10,715
H5-7	9	6	2	3	8	60	15	11,296	60	10,599

Note: **Bold** type indicates relatively fresh parent material.

TABLE 5
Comparison between Selected Extractable and Total Metal Concentrations for Selected Samples (mg/kg)

Samples	V (t) ^a	V (ex) ^b	Cr (t)	Cr (ex)	Zn (t)	Zn (ex)	Cu (t)	Cu (ex)	Pb (t)	Pb (ex)	Mn (t)	Mn (ex)	Fe (t)	Fe (ex)
S1-1	23	14	14	3	54	32	1	1	3	3	26	17	4,500	1,169
S1-2	75	41	42	15	53	11	1	1	12	8	38	3	71,300	36,149
S1-3	67	13	30	5	67	38	9	9	13	10	20	20	53,000	27,048
S1-4	18	3	8	1	32	14	7	3	6	4	5	5	5,400	2,146
S1-5	53	9	29	4	138	117	15	14	17	15	309	262	36,000	17,882
B3-1	43	9	37	3	126	103	5	5	13	9	651	620	24,000	13,014
B3-2	22	9	10	3	52	34	3	3	7	5	578	550	35,500	23,680
B3-3	38	12	25	5	67	46	4	3	9	7	814	755	18,400	12,119
B3-4	43	20	20	7	64	49	4	4	10	7	1,274	1,200	41,300	26,411
GB1-1	18	4	19	5	61	25	3	2	6	3	17	8	2,900	822
GB1-2	381	284	725	352	78	69	63	56	17	6	122	50	73,000	38,226
GB1-3	290	201	842	475	96	93	60	54	7	4	180	65	243,200	119,736
GB1-4	360	70	277	53	100	95	86	84	6	3	177	35	50,300	14,893
GB1-5	63	26	75	27	111	86	16	10	12	7	120	69	32,400	15,694

^a (t), total element content (HF).

^b (ex), readily extractable element (aqua regia).

TABLE 6
Mineralogy of Weathered and Fresh Rocks (%) by X-Ray Diffraction Method

Sample	Quartz	Feldspar	Kaolinite	Mixed Layer I/S	Illite	Hematite	Siderite	Calcite
S1-1	78.9	0.7	18.9	1.5	0.0	nd	nd	—
S1-2	39.0	0.9	42.9	9.7	3.7	3.9	nd	—
S1-3	32.0	2.4	30.1	21.5	10.5	3.6	nd	—
S1-4	85.0	5.4	3.7	3.3	2.6	nd	nd	—
S1-5	64.8	6.9	17.2	6.0	3.5	nd	1.7	—
B3-1	55.8	16.2	12.8	8.3	2.7	1.1	3.0	—
B3-2	65.3	14.5	8.0	3.8	2.5	1.1	4.8	—
B3-3	62.2	15.2	10.7	4.2	3.5	nd	2.5	1.7
B3-4	57.0	16.3	11.4	5.3	3.9	nd	5.3	0.8
B7-1	72.8	6.7	16.5	1.9	2.1	nd	nd	—
B7-2	70.4	15.1	12.0	1.9	0.6	nd	nd	—
B7-3	79.6	15.1	5.3	Traces	Traces	nd	nd	—
B7-4	53.9	37.3	2.2	1.3	5.3	nd	nd	—
L1-1	82.7	1.1	15.6	0.0	nd	0.7	nd	—
L1-2	88.1	0.5	11.0	nd	nd	0.3	nd	—
L1-3	86.7	0.3	12.3	nd	0.1	0.7	nd	—
L1-4	82.3	0.8	13.8	nd	1.9	1.2	nd	—
L1-5	50.7	6.8	16.5	6.4	13.4	0.7	5.6	—
GB1-1	96.3	0.4	2.5	nd	0.1	0.7	nd	—
GB1-2	54.9	0.8	42.4	nd	nd	1.9	nd	—
GB1-3	19.4	1.0	68.6	nd	6.1	4.9	nd	—
GB1-4	2.6	15	80.2	nd	nd	2.2	nd	—
GB1-5	61.0	15.7	9.4	3.6	9.3	0.9	nd	—
H5-1	49.5	0.7	41.6	5.9	nd	2.4	nd	—
H5-2	55.9	1.0	31.2	9.5	nd	2.5	nd	—
H5-3	55.5	1.4	34.3	6.1	nd	2.6	nd	—
H5-4	76.7	1.1	14.9	4.2	nd	3.2	nd	—
H5-5	60.2	1.3	25.3	11.2	nd	2.0	nd	—
H5-6	68.9	1.5	21.9	4.1	2.7	0.9	nd	—
H5-7	50.8	2.8	25.0	16.0	3.5	1.7	nd	—

Note: **Bold** type represents fresh rock. nd, not detected (<0.5% for primary minerals and <1% for clay minerals). —, no analysis.

helps assess the potential further release of such metals from weathered bedrock. Both methods of digestion (extractable and total) were applied for selected samples to compare the amount of trace elements contained in silicate structures with those weakly adsorbed and easily extractable. Fourteen samples were selected (four to five samples from three cores) to cover the whole range of values identified by *aqua regia*.

Mineralogical Composition

The primary minerals identified in the study area are quartz (2–96%), plagioclase (1–32%) and K-feldspar, which occurs in only five samples (3–10%); secondary minerals

are kaolinite (0–67%), mixed layers of smectite-illite (0–22%), illite (0–14%), hematite, goethite, siderite, and calcite (Table 6). Overall, parent rock silicates have been extensively replaced by clay minerals and Fe oxides (mainly hematite).

Spatial variation of mineralogical content was studied in cores S1, H5, and L1 (Figure 3). Cores S1 and H5 are mineralogically comparable, but core L1 is substantially different compared with other cores discussed earlier. The most abundant primary mineral is quartz, and the clay content decreases upward (Table 6, Figure 3). Other cores such as B7, B3, and GB1 clearly demonstrate a range of vertical variations within weathered profiles (Figure 4).

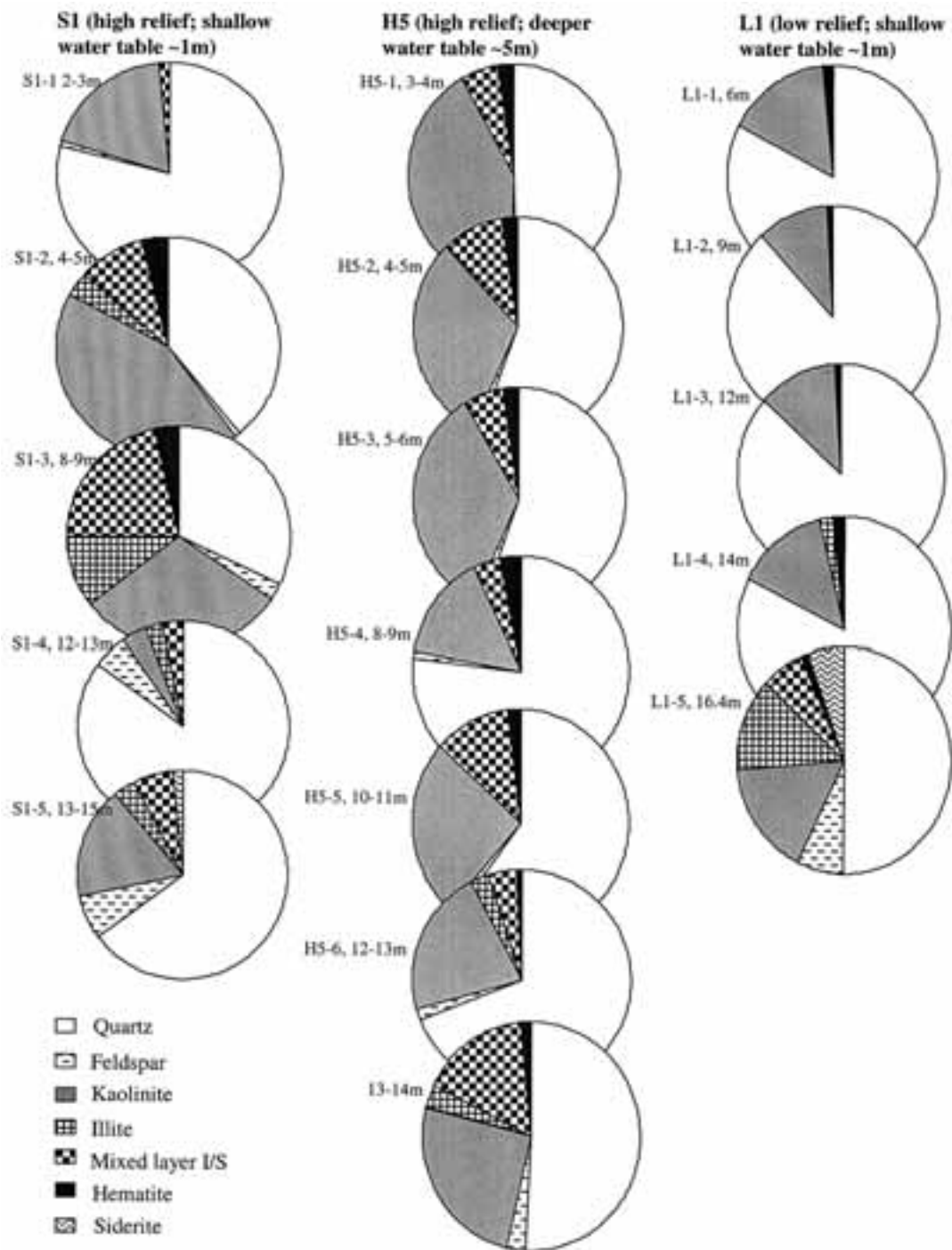


FIGURE 3. Spatial variations in mineralogy between bore holes developed on mudstone. S1 and H5 are both located on a higher relief. S1 is more leached compared with H5 due to its shallow water table. Although the water table occurrence in core L1 is similar to that in S1 (1 m below the surface), the degree of weathering and leaching in L1 is higher than in S1 because the former is located on a flat terrain.

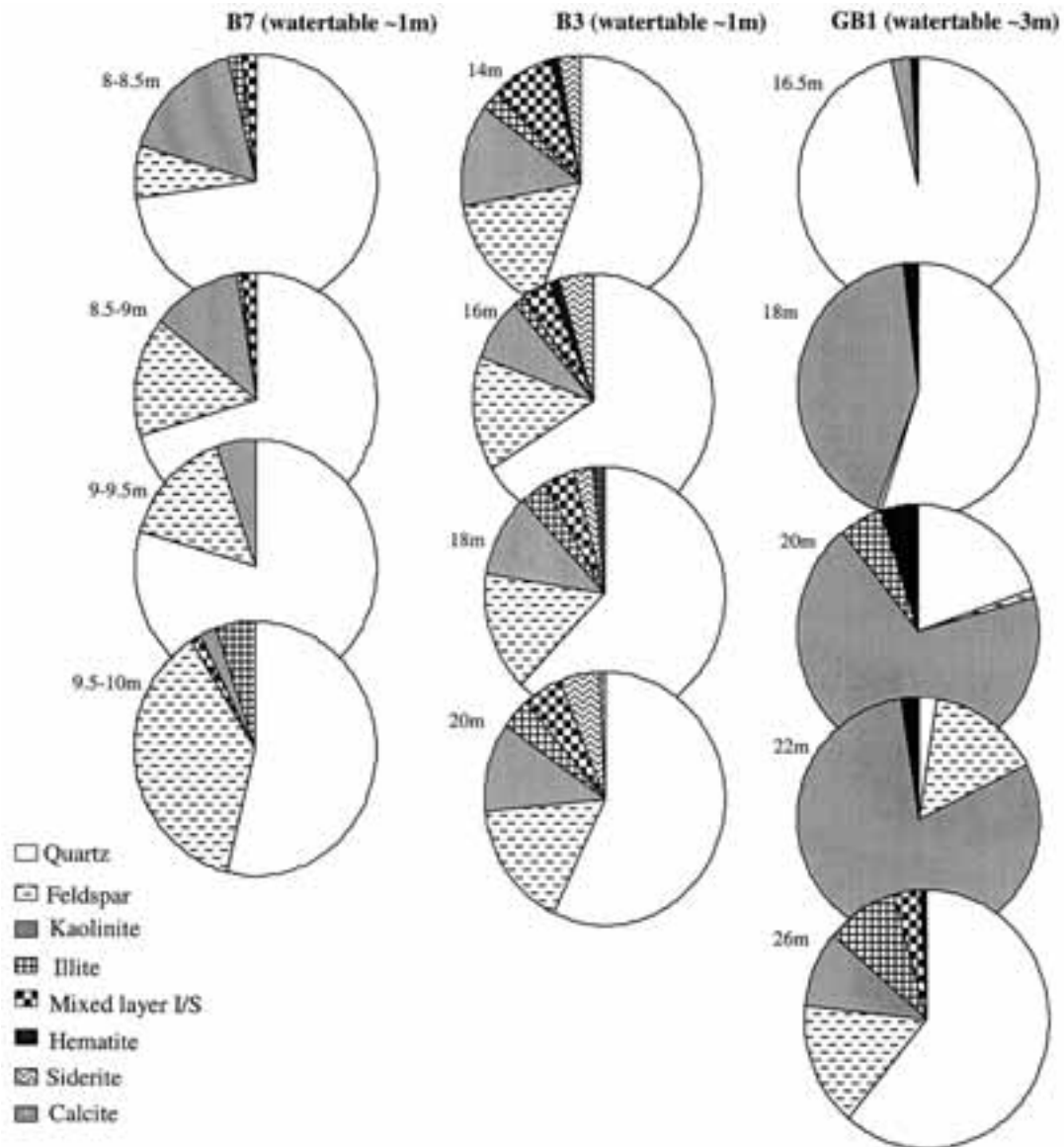


FIGURE 4. Vertical variations in mineralogy showing that deeper layers are fresher with higher primary mineral content. Both B7 and B3 are developed on sandstone bedrock, but GB1 shows a weathered profile within mudstone-dominated bedrock. The higher clay amounts in GB1 compared with B7 and B3 show this difference between parent rocks.

DISCUSSION

Relationship between Total and Extractable Components

The lower values of extractable V and Cr content compared with total digestion indi-

cate that they are part of the aluminosilicate matrix and from an environmental prospective are not readily releasable. Metals such as Cu, Zn, and Pb, however, are mostly adsorbed to particles and easily leached and available to the environment. Manganese

does not show consistent behavior and only has high extractability where its concentration is high (up to 95% recovery). Iron occurs in primary minerals (lithic fragments of volcanic origin have been reported by Cranfield [1983] and Hawkins [1983]) and as insoluble secondary iron phases such as hematite (Table 6). A comparison between total and extractable iron (Table 5) shows that its extractability varies between 30 and 65%, suggesting that the remaining iron is in primary mineral structures and can undergo further release during weathering.

Relationship between Mineralogy, Geological Setting, and Chemical Composition of Weathering Profiles

Six distinctly different weathering profiles were identified at the top of the parent bedrock in Bells Creek catchment and vary in thickness between 10 and 26 m. The study of mineral and chemical composition shows that the spatial variation of mineralogical content is controlled by topography and position of water table (Figure 3) and also relates to the composition of parent rock (Figure 4).

Drill holes S1 and H5 are both located in slightly undulating weathered bedrock hills and are mineralogically comparable, but core L1 is situated on a flat terrain. In profiles S1 and H5, the albite is the dominant plagioclase observed; its amount decreases upward, while the kaolinite content increases, indicative of intense weathering and leaching (e.g., Chamley 1989). Core S1 contains less cation-rich clays such as mixed layers and hematite at the top of the profile. Because these minerals are the main scavengers for trace elements, average trace metal content relative to parent material for core S1 is much lower compared with drill hole H5 (Figure 5). The differences could be related to the fact that in core S1 the water table (determined by ground-penetrating radar) was just below the surface, but in H5 it was located well below 5 m. In drill hole L1 the water table occurred 1 m below the surface, and although the mudstone bedrock contains 36% clay minerals (Table 5) in the upper part of the profile the amount of clays substantially decreases (e.g., at 9 m

depth L1-2 contains only 11% kaolinite). A comparison between metal contents of core L1 with S1 and H5 confirms that lower clay mineral content contributes to low metal content in core L1. In addition, comparisons between these three cores reveal that material located on flat terrain with a shallow water table (e.g., L1) weathers to a greater extent than cores located in undulating hills (Figure 3). Shallow groundwater is also associated with low concentrations of trace metals, suggesting that subsurface water flow is an important mobilizing factor (Figure 6).

Core B7 is comparable with B3 because samples taken from them occur 7–14 m below paleofluvial channels and have developed on sandstone. Mineralogical data show that B7 with a shallow water table is more weathered than B3 because it contains higher amount of quartz (up to 80%) and only 6.6% of feldspars (Table 5). Core GB1 contains the most weathered material encountered and the compositions of the samples taken from this core clearly demonstrate the different phases of weathering and leaching operating in this system (Figure 4). The presence of higher feldspar content in GB1-5 (16%) indicates a fresher rock, and the development of kaolinite from GB1-4 to GB1-3 suggests alteration of silicate minerals. From GB1-2 to GB1-1 the transition from weathered zone to completely leached zone is clearly illustrated (Figure 4). Core GB1 is the most suitable core for the study of vertical distribution of trace elements with regard to weathering and mineralogical content. In GB1-1 there is a substantial decrease in trace element contents due to extreme leaching compared with the other three samples from this core.

One of the initial assumptions was that the setting (i.e., nonchannel or channel) could have an influence on the weathering. The study shows that metal concentration of shallow profiles (e.g., S1) does not differ from that of profiles developed under thick layers of unconsolidated material (e.g., H5). It can therefore be concluded that the effect of depth of burial of the weathered profile is insignificant compared with mineralogy.

The presence of kaolinite in all the samples (up to 69%) is indicative of intense

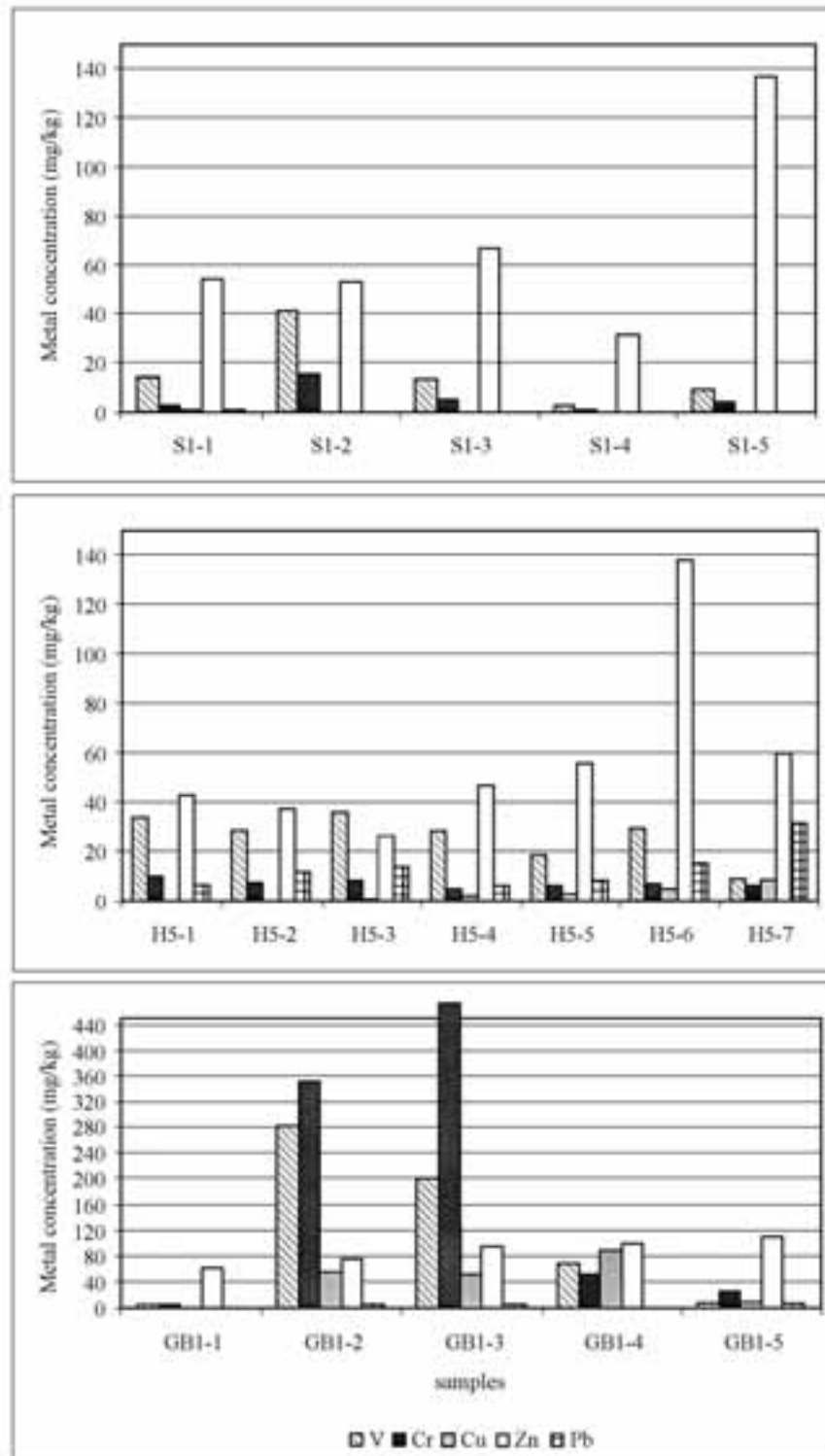


FIGURE 5. Vertical variation of metal distribution with regard to mineralogy (Figures 3 and 4).

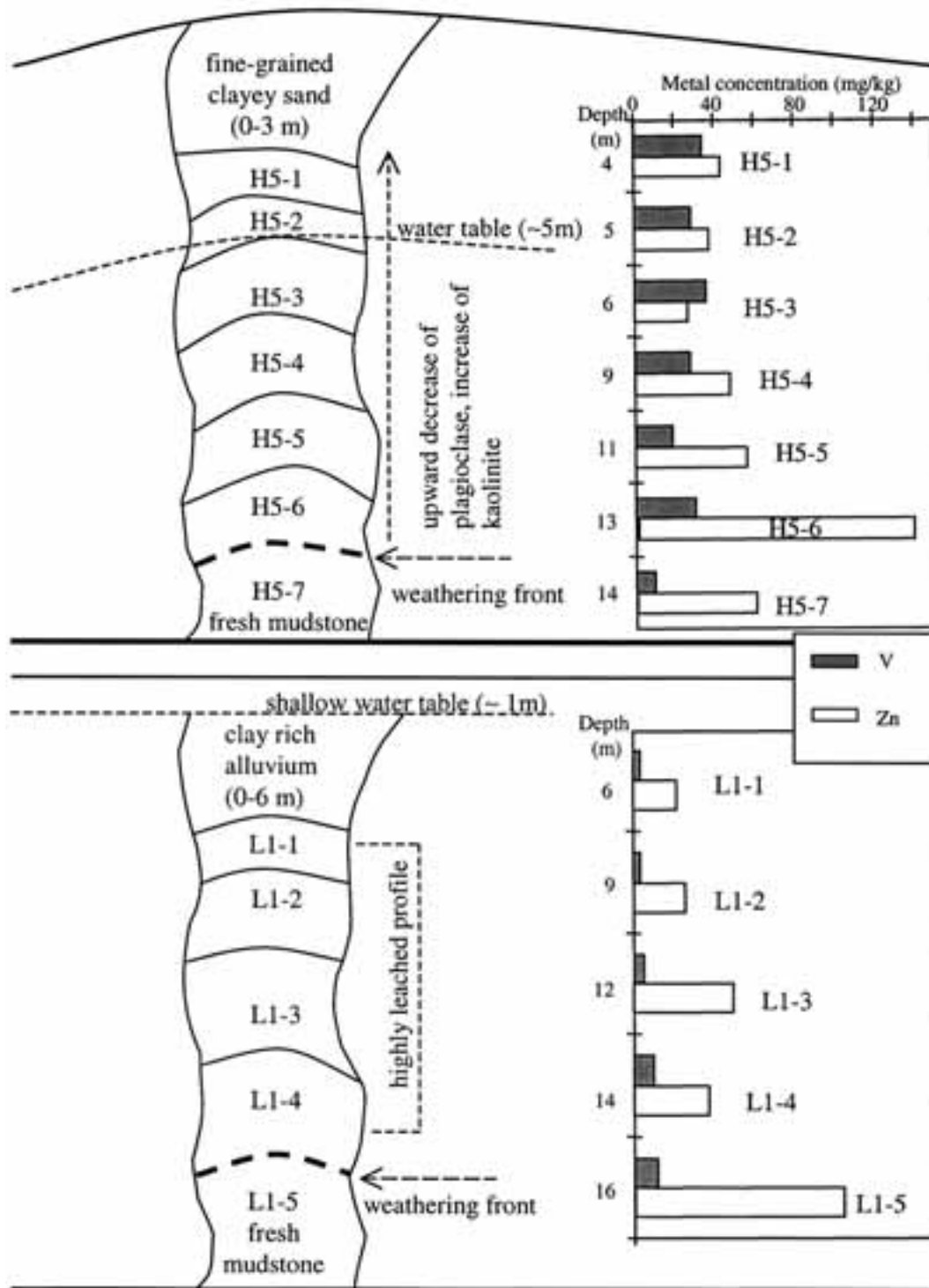


FIGURE 6. Schematic representation (not to scale) of effect of relief and water table position on two typical weathered profiles. Profile H5 is located on an undulating weathered hill with deeper water table and shows a limited degree of weathering. Profile L1 is located on a flat terrain with water table occurring 1 m below the surface. Metal distribution is shown to be related to degree of weathering.

TABLE 7
Spearman's Rank Correlation Matrix for Weathered Material ($n = 26$)

	V	Cr	Cu	Zn	Pb	Fe	Mn	Al	Quartz	Feldspar	Kaolinite	Illite	Mixed Layer	Hematite
V	1.0													
Cr	0.8	1.0												
Cu	0.2	0.3	1.0											
Zn	0.2	0.3	0.8	1.0										
Pb	0.2	0.3	0.3	0.4	1.0									
Fe	0.7	0.6	0.4	0.4	0.4	1.0								
Mn	0.0	0.1	0.7	0.7	0.3	0.3	1.0							
Al	0.7	0.8	0.2	0.1	0.2	0.5	-0.2	1.0						
Quartz	-0.7	-0.7	-0.4	-0.4	-0.4	-0.6	-0.2	-0.6	1.0					
Feldspar	-0.1	0.0	0.6	0.5	0.5	0.2	0.7	-0.3	-0.3	1.0				
Kaolinite	0.8	0.7	0.2	0.1	0.2	0.5	-0.2	0.9	-0.8	-0.2	1.0			
Illite	-0.1	0.1	0.5	0.6	0.4	0.3	0.6	-0.2	-0.3	0.5	-0.2	1.0		
Mixed Layer	0.2	0.1	0.0	0.2	0.8	0.3	0.2	0.1	-0.5	0.4	0.3	0.3	1.0	
Hematite	0.6	0.6	0.0	-0.1	0.2	0.6	-0.2	0.7	-0.6	-0.2	0.7	-0.1	0.3	1.0

Note: **Bold** type shows strong correlation. 0.60–1.00 = strong correlation; 0.50–0.59 = moderate; 0.40–0.49 = weak; 0.00–0.39 = little or no association.

weathering. Although the intensity of weathering for almost all the profiles is intense to extreme (60–100%) (unpubl. data), gibbsite, which is often associated with advanced weathering, was not found in any of the profiles. Gibbsite commonly occurs with kaolinite in tropical areas and is a major end product of weathering of aluminosilicate minerals. In some areas an abundance of moisture and good drainage contribute to formation of crystalline gibbsite (e.g., Evans 1992); in other regions, relatively higher elevation and more than 7,000 mm/yr of precipitation (e.g., Islam et al. 2002) or deep weathering fronts (e.g., Calvert et al. 1980) create conditions favorable for forming a kaolinite-gibbsite-goethite suite through weathering of feldspars. Gibbsite has not formed in the weathered profiles studied presumably due to insufficient moisture and drainage, because the study area is relatively low lying with an average yearly precipitation of only 1,400 mm. However, traces of gibbsite could have been present but in quantities undetectable by X-ray diffraction.

The mineralogical study revealed siderite and occasional calcite in cores S1, B3, and L1. In general, siderite occurrence is due to diagenetic processes under high temperature and pressure (Berner 1971, Mozley and Wer-

sin 1992, Taylor 1998, Uysal et al. 2000); in the case in the Bells Creek catchment, it is more likely that siderite and calcite have both precipitated in rock fractures from carbonate-rich pore water. The scarce occurrence of carbonates did not allow for speculation on the influence of these minerals on metal distribution/mobility.

Correlations between Mineralogy and Trace Metal Distribution

Spearman's rank correlation matrix enabled the identification of relationships between metals and potential inorganic scavengers influencing metal mobility and distribution within weathered material (Table 7). Based on the correlation matrix, concentration of V and Cr is predominantly controlled by kaolinite. However, the primary control over Cu and Zn concentration is Mn, followed by illite; Pb correlated only with mixed layers of illite-smectite.

A comparison between pie graphs (Figures 3 and 4) representing mineralogy of the drill holes with trace metal concentrations (Figure 5) confirmed the interpretation based on the correlation matrix. Although the concentration of metals such as V and Cr is primarily controlled by kaolinite, other scavengers

such as Fe, Al, and hematite also influence their occurrence and distribution. As shown by Figures 4 and 5, highest concentration of V and Cr occurs in core GB1-3 with almost 70% kaolinite content and 5% hematite (the highest in this core). This finding demonstrates that although kaolinite concentration was up to 80% in GB1-4, V and Cr concentrations were lower than in GB1-4 perhaps due to high concentration of feldspars in GB1-4. For elements such as Pb the dominant influence of mixed layers of illite-smectite as scavenger can be observed in Figures 3 and 5. These figures show that highest concentration of Pb (32 mg/kg) occurs at H1-7, with the highest mixed layer content of 16%. The effect of clay minerals on Zn is not obvious from Figures 3–5 because concentration of this element is predominantly correlated with Mn concentrations (Table 7).

Overall, profiles with lower abundances of secondary minerals contain lower concentrations of metals, as clay minerals and hematite are the main scavengers for trace metals. Furthermore, mineralogical data confirmed more intense weathering occurs on flat terrains compared to undulating hills. Although weathering is intense to extreme for most profiles (Liaghati, Preda and Cox, unpubl. data), gibbsite was not detected in the study area possibly due to insufficient moisture and drainage. The areas, which are more prone to leach metals, are morphologically flat with a shallow water table and mudstone as parent rock. The relative influence of mineralogy, geological setting, and groundwater occurrence and flow on chemical weathering of the sedimentary rocks in this catchment has been found to be: mineralogy > geological setting (topography & parent rock type > water table depth > depth of profile burial).

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