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AN ABSTRACT OF THE THESIS OF Joseph Michael Fassio for the
Master of Science in Geology presented June 7, 1990

Title: Geochemical Evolution of Ferruginous Bauxite Deposits
in Northwestern Oregon and Southwestern Washington

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Ferruginous bauxite deposits developed from flows of the Columbia River Basalt Group in northwestern Oregon and southwestern Washington. Samples of the iron pisolite and the gibbsite nodular zones from the upper portion of the weathering profile of drill core from Columbia County, Oregon and Cowlitz County, Washington, were analyzed by

instrumental neutron activation. The mineralogy was determined using X-ray diffraction and Mössbauer spectroscopy.

The gibbsite nodular zone is above the clay-rich saprolite or relic basalt zone. The nodules contain relic vesicles and well preserved relic plagioclase microlites. Gibbsite occurs with poorly crystalline goethite and hematite in the gibbsite nodular zone. Clays are absent in this part of the profile.

The iron pisolite zone is at the top of the profile above the gibbsite nodular zone. Both maghemite and goethite pisolites occur in the lower part of the zone while maghemite pisolites are dominant in the upper part of the pisolite zone.

The parent flow is the Frenchman Springs Member of the Wanapum Basalt for the Columbia County profile and the Pomona Member of the Saddle Mountains Basalt for the Cowlitz County profile.

Distribution of the major, minor and trace elements through the profile shows three distinct sympathetic patterns consisting of lanthanide elements and Na; As, Sb, Th, Hf, and Ta; and transition metals Fe, Ti, V, and Cr.

Ratios between the high-field strength elements Ta and Hf are nearly constant through the profile, and Hf appears to be the least mobile elements of the elements analyzed in the profile. Ratios of other elements were calculated against Hf, based on the assumption that it has remained largely immobile during weathering, to show element enrichment and depletion in the profile independent of mass-volume changes. Transition metals and Al show a progressive depletion through the upper gibbsite nodular and iron pisolite zone due to leaching in the

profile. Lanthanide elements (except Ce), As, and Sb show an obvious enrichment in the iron pisolite zone relative to the gibbsite nodular zone.

Volume reduction during weathering was calculated based on the immobility of Hf. In the gibbsite nodular zone, the volume reduction calculated for bulk samples is greater than for gibbsite nodule separates suggesting that a greater volume reduction occurred the matrix material surrounding the nodules. Ratios between gibbsite nodules and parent basalt of the immobile elements Hf, Ta, Fe, Ti, Th and Cr suggest that the nodules, where the relic textures are preserved, have undergone volume reduction. Based on the immobility of Hf, the gibbsite nodules lost approximately 40% of the original volume. The volume factors based on the immobility of Hf show that the pisolite zone experienced a greater volume reduction than the gibbsite nodular zone.

Absolute gains and losses relative to the parent basalt show the following relative order of depletion: $\text{Na} > \text{La} > \text{Eu} > \text{Sm} > \text{Co} > \text{Mn} > \text{Ce} > \text{Sc} > \text{Ta} > \text{V} > \text{Cr} > \text{Lu} > \text{Th} > \text{Fe} > \text{Ga} > \text{Al}$. The lesser mobility of Ce and Lu relative to other lanthanide elements suggests fractionation of lanthanide elements in the bauxite profile. Aluminum is both enriched and depleted at different depths in the gibbsite nodular zone suggesting that Al is mobilized from the matrix and possibly the pisolite zone into Al enriched gibbsite nodules.

Volume reduction and destruction of relic textures in the pisolite zone is accompanied by small-scale mobilization of Th, Cr, Fe, Hf, Ga, Sc, and Ta during the formation of iron pisolites.

Formation of the iron pisolite zone above the gibbsite nodular

zone may indicate a change in climate from a heavy year round to a seasonal rainfall pattern.

GEOCHEMICAL EVOLUTION OF FERRUGINOUS BAUXITE DEPOSITS
IN NORTHWESTERN OREGON AND SOUTHWESTERN WASHINGTON

by

JOSEPH MICHAEL FASSIO

A thesis submitted in partial fulfillment of the
requirements for the degree of

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in
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1990

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I would like to dedicate this thesis to my wife Erin who contributed unending support and encouragement.

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INTRODUCTION

GENERAL

Bauxite is the end product of intense chemical weathering of rock and, relative to the parent rock, is enriched in iron and aluminum while depleted in silica and the alkali metals. Beside the obvious economic importance as a source of aluminum, bauxites and laterites are important sources of nickel, gallium, niobium, and lanthanide elements (Mariano, 1989).

Details of geochemical processes during the formation of bauxite are poorly understood. During weathering of the parent rock, leaching of major elements, such as silica, causes significant mass and volume changes which result in the relative enrichment of major, minor and trace elements. On the other hand, absolute enrichment is the result of colloidal or solution transport of elements in the vadose and saturated zones followed by later precipitation. Without a knowledge of parent rock composition, analysis of relative and absolute concentration changes cannot be rigorously accomplished. When determining the enrichment and depletion of elements in the bauxite profile, few studies know the element concentration in the parent materials (diabase, Schorin and Puchelt, 1987; andesite, Chen et al., 1988; basalt, Pattan and Appangoudar, 1988) and even fewer take into account mass-volume changes that occur during weathering (Duddy, 1980; Eggleton et al., 1987).

Partitioning of trace elements among coexisting textural components or mineral phases in intensely weathered profiles has received little attention. Iron pisolites that form in hard pan layers in temperate zone lateritic soils represent a local absolute enrichment of iron as accumulations of Fe-Al oxides and oxyhydroxides (Nahon, 1986). Little is known or documented about what trace elements, if any, are enriched with iron during the growth of a pisolite. Iron phases, particularly the oxyhydroxides, have an important role in scavenging trace elements in soils (Jenne, 1977).

Northwestern Oregon and southwestern Washington have several areas where bauxite deposits have developed from flows of the Columbia River Basalt Group (CRBG). Studies by Jackson (1974), Hoffman (1981), and Marty (1983) established the stratigraphic relation between the bauxite and the parent flows.

This study focuses on the upper portion of the ferruginous bauxite profile, the gibbsite nodular and iron pisolite iron zones. The purpose of the study is:

1. to determine the changes in major, minor, and trace element concentrations from parent rock to weathered material in the bauxite profile.
2. to distinguish elements concentrated due to mass/volume changes from those concentrated by chemical migration.
3. to compare and contrast the distribution of elements in the profile at different sites.
4. to determine the partitioning of elements between the secondary iron pisolites and matrix in the iron pisolite zone at the top of the

bauxite profile.

PREVIOUS WORK

The best constrained studies on the behavior of elements during weathering are those where fresh, unweathered rock or corestones and derived saprolite have been studied (Nesbitt, 1979; Duddy, 1980; Colman, 1982; Eggleton, et al. 1987; Middelburg et al., 1988). Chemical gradation between fresh rock and saprolite can be more easily measured in corestones than in soil profiles. In more intensely weathered saprolites enrichment of elements due to either mobility or residual concentration is more difficult to determine because of volume changes.

Most work on the geochemistry of bauxite and laterites has concentrated on changes in bulk mineralogy through the weathering profile. Kronberg et al. (1979, 1982) found that the dominant clay minerals in Brazilian laterites control the trace element behavior. The section in the Brazilian laterite profile that contains montmorillonite and illite group minerals retain higher concentrations of trace elements than the section in the same profile with kaolinite and gibbsite. Chen et al. (1988) documented a wholesale depletion of alkali metals and Si relative to the parent andesite where gibbsite forms at the expense of clay minerals. Topp et al. (1985) found considerable enrichment of rare earth elements deeper in the weathering profile. Lanthanum, Ce, Sm, and Eu were concentrated in a hematite-rich zone in the profile. Schorin and Puchelt (1987), and Pattan and Appangoudar (1988) characterized depletion relative to parent rock material. These studies of bauxites and laterites, however, do not determine whether enrichment is due to

mass/volume changes or to mobility.

Few studies attempt to decipher details of the fractionation of trace elements within laterite and bauxite profiles. Dennen and Norton (1977) separated the less than 200 mesh size fraction from gibbsite and iron nodular concretions and found a greater affinity of trace elements for the iron oxide pisolites and fine-grained fraction (less than 200 mesh size) than gibbsite nodules. Topp et al. (1985) chemically extracted the Fe and Al-rich fractions and found that trace elements were mainly associated with the Fe-rich fraction.

In the Northwest, Libbey et al. (1945), Allen (1948), and Corcoran and Libbey (1956) studied the geology and geochemistry of ferruginous bauxite in Oregon. Livingston (1966) conducted a similar study in Washington. Hook (1976) evaluated the economic potential of the bauxite in the Pacific Northwest. He estimated reserves at 57 million metric tons.

Graduate students at Portland State University (Jackson, 1974; Hoffman, 1981; Marty, 1983) conducted studies of the geology, mineralogy, and geochemistry of Washington and Oregon ferruginous bauxite. Jackson (1974) examined the geochemical and mineralogical changes from fresh basalt core stones to bauxite. Hoffman (1981) and Marty (1983) examined stratigraphic relations between the bauxite deposits and parent flows of the CRBG in the Salem Hills and Columbia County, respectively.

OCCURRENCE OF BAUXITE DEPOSITS IN THE PACIFIC NORTHWEST
AND THE LOCATION OF THE STUDY PROFILE

Ferruginous bauxite deposits in the Pacific Northwest occur in scattered areas in Columbia, Washington, Multnomah, Yamhill, Clackamas and Marion Counties in Oregon and in Cowlitz and Wahkiakum Counties in Washington (Figure 1). The bauxites occur where flows of the CRBG and inter-flow sediments once capped the broad flat-top ridges and uplands in the Coast Range province. Exposures of bauxite are rare. Vertical and aerial extent were estimated from core hole data and topographic expression (Livingston, 1966; Hook, 1976). In Washington's Wahkiakum and Cowlitz Counties, bauxite underlies the ridges above the Columbia River between the towns of Kelso and Cathlamet. In Columbia County, Oregon, bauxite occurs on the ridges west of St. Helens and Columbia City. The bauxite in Oregon's Washington County caps Pumpkin Ridge and Dixie Mountain, and the deposits in Multnomah County cap the Portland Hills. Deposits in Marion County occur within the city limits of Salem and in the Salem-Eola Hills south of the city. Laterites at Mehama in Marion County and Estacada in Clackamas County may have developed from a tuff younger than the CRBG (Hook, 1976).

Concern during the 1940's, 1950's and early 1970's over the availability of strategic metals such as aluminum prompted exploration by government agencies and private corporations. Reynolds Metals Company and Alcoa Mining Company drilled 6,898 test holes on lease holdings (Hook, 1976). Cores from holes drilled by Reynolds Metals Company in the early to mid-1970's were released to the Oregon

Figure 1. Map of occurrences of ferruginous bauxite in the Pacific Northwest. Modified from Livingston (1966).

Department of Geology and Mineral Industries and Portland State University in 1989. Reynolds drilled the cores in a closely spaced grid pattern at locations in Columbia and Washington Counties in Oregon, and Wahkiakum and Cowlitz Counties in Washington. The depth of the cores ranges between 4 and 15 m. Two cores were selected for this study. One is from a profile in the NW 1/4 of SEC 31, T.9N., R.3W. (hole # 9/1 31 2C) at an approximate elevation of 230 m in Cowlitz County, Washington, 4.4 km north of the town of Stella. The second core was drilled in Columbia County, Oregon approximately 2.7 km west of Columbia City off Smith Road in SEC 19, T. 5 N., R. 1. W. (hole # 5/1 19 3A) at an elevation of about 200 m.

GEOLOGIC SETTING AND THE BAUXITE STRATIGRAPHY

Libbey et al. (1945) first used the term ferruginous bauxite to describe the deposits in western Oregon and Washington. Valetton (1972) includes ferruginous bauxite in a ternary classification of bauxites and aluminous iron ores and clays. The classification scheme is based on the percentage of allitic minerals (gibbsite, nordstrandite, boehmite, diaspore and corundum), ferritic minerals (goethite, lepidocrocite, hematite, magnetite, and maghemite), and clay minerals (mostly kaolinite). A ferruginous bauxite contains 50 to 75% allitic minerals, 25 to 50% ferritic minerals, and less than 15% clay minerals.

Ferruginous bauxite in the Pacific Northwest is weathered from flows of the Miocene CRBG and minor interflow sediments. The CRBG has been subdivided into formations; the Saddle Mountains, Wanapum, Grande Ronde, and Imnaha basalts. Distribution of flows has been mapped based on geologic field relations, paleomagnetic properties, and geochemistry. Chemically, flows have been differentiated by the concentrations of major and minor elements such as TiO_2 , FeO , and MgO , and trace elements such as Cr, Sc, and Th. Unweathered basalt is typically dark gray to black, dense, and fine grained with a hyalo-ophitic texture. In thin sections, the rocks contain 30-40% glass, 40-45% plagioclase, 25-30% augite, less than 10% opaques, and less than 1% olivine. Most of the plagioclase occurs as microlites, and less than 1% occurs as

phenocrysts. In Columbia and Cowlitz counties, the CRBG unconformably overlies the late Eocene to early Oligocene Goble Volcanics, Eocene Cowlitz Formation, and Oligocene age sediments. A poorly consolidated siltstone unit called the Portland Hills Silt in Columbia County unconformably overlies the CRBG. The silty units described by Livingston (1966) in Cowlitz and Wahkiakum Counties are called post-Troutdale silty clay.

Walsh (1987) mapped the Frenchman Springs Member of the Wanapum Basalt and the Pomona Member of the Saddle Mountains Basalt in Cowlitz County in the area where the bauxite cores were drilled by Reynolds Metals Co. The CRBG in Columbia County, mapped by Wilkinson et al. (1946), has not been subdivided into formations and members. The Pomona and Frenchman Springs members are 12 and 15.3 Ma in age respectively (Tolan et al., 1989).

When laterization occurred is uncertain. Age is constrained by the Miocene CRBG and the deposition of the Portland Hills Silt during the late Pleistocene. The Portland Hills Silt was dated at between 34,000 and 700,000 B.P. by carbon-14 dating (Glenn, 1965). Livingston (1966) suggests that considering the present climate, topography, and vegetation of western Oregon and Washington laterization processes may be continuing today.

Although ferruginous bauxite developed from the CRBG, in most areas, basalt crops out without the overlying bauxite. The spotty distribution of bauxite is somewhat puzzling. Most workers agree that conditions favoring a high water-to-rock ratio are the requisite for laterization. Libbey et al. (1945) and Corcoran and Libbey (1956)

believed that ferruginous bauxite developed like a blanket over all exposed locations of the CRBG. Erosion subsequently removed the bauxite in most areas. However, drill hole data (Hook, 1976) and field evidence (Marty, 1983) show complete sections of basalt without bauxite development, which contradicts the blanket theory. Hook (1976) found that the thickness of laterite increases toward the lower portions of the dip slopes cut by deep stream valleys. Hook suggested that the laterization commenced sometime after the development of the 'youthful' topography of the dip slope. Bauxite development may have been controlled by the chemical and physical characteristics of the parent rock. Hoffman (1981) found that bauxite in the Salem Hills area of Marion County formed almost exclusively on the Kelley Hollow flow of the Frenchman Springs Member. However, the texture and chemistry of the parent does not strictly control laterization. Marty (1983) found that bauxite formed on flows of the Grande Ronde Basalt as well as flows of Wanapum Basalt. He also found that bauxite deposits were thickest over areas with fault zones and suggested those were areas of more intense leaching due to the greater permeability of groundwater through the structural zones.

Hook (1976) subdivided the ferruginous bauxite section into the relic basalt, fine-grained, nodular, and pisolitic zones (Figure 2). Hook described the relic zone as a soft, varicolored, clay-rich saprolite up to 34 m thick with an average thickness of 6 m. This zone is transitional between the unweathered basalt and the ferruginous bauxite. Drilling shows that the weathering profile can be very deep. The Dudley Deep no. 20 test core drilled by Alcoa Mining Co. in 1946 in

Thickness		Zone	Composition	Profile	Description
range	average				
In feet	0 - 50	20	Silty Clay Overburden		Tan silt, loose, soft; grades to red silty clay, dense, plastic, with thin silt beds
	0 - 9	4	Pisolitic Zone		Pisolitic clay, durable, friable
	0 - 40	12	Nodular Zone		Hard gibbsitic and limonitic nodules or fragments, subrounded to angular
			Fine-grained Zone		Fine-grained, brown, ferruginous bauxite with magnetite and ilmenite crystals
	0 - 40	20	Upper Relic Basalt Zone		Varicolored, soft clay with relic basalt texture. Some spheroidal weathering with occasional hard basalt boulders at center of spheroids. Manganese oxides increase toward bottom.
	0 - 110+	?	Lower Relic Basalt Zone		Clay-altered basalt, dark-gray to brownish with orange to pink halloysite and black manganese oxides in joints. This zone is generally a firm saprolite but may have hard, unaltered basalt boulders.
			Basalt		Hard, black basalt

Figure 2. Generalized section of ferruginous bauxite. From Hook (1976).

NW 1/4 of SEC 5, T.2 N., R.2 W. in Washington County, Oregon penetrated 46 m of weathered profile before encountering fresh basalt. The relic zone generally has a lower density than the unweathered basalt below and the ferruginous bauxite above. Although smectite, illite, and chlorite occur in the lower part of this zone, the clays are predominately kaolinite and 7Å-halloysite. Hard unweathered basalt spheroids, or corestones, are found throughout this part of the section. The composition averages 26% Al_2O_3 , 28% Fe_2O_3 , 29% SiO_2 , 19% LOI (Loss on ignition) (Hook, 1976).

Together, the fine-grained and nodular zones constitute the high-alumina, low-silica bauxite ore. Because of their mineralogical similarities and uneven contact, Hook (1976) combined the fine-grained and nodular zones into a single unit with a total average thickness of about 3 m and a maximum thickness of 13 m. The fine-grained zone is massive, fine grained and dark brown with a high percentage of gibbsite. The nodular zone is characterized by hard angular to subrounded gibbsite-rich nodules surrounded by reddish-brown matrix. The average composition of the fine-grained and nodular zone is 38% Al_2O_3 , 32% Fe_2O_3 , 4% SiO_2 , 20% LOI (Hook, 1976).

The pisolitic zone contains iron-rich, dark brown to black pisolites in a reddish brown matrix. The average thickness is one meter. The pisolites often contain grains of quartz. Jackson (1974) believed that the quartz grains were detrital in origin. Marty (1983) found no evidence for reworking of the material in the pisolite section and concluded that the quartz was pedogenic. The average composition of the pisolite zone is 37% Al_2O_3 , 22% Fe_2O_3 , 18% SiO_2 , and 19% LOI (Hook, 1976).

PHYSICAL CHARACTERISTICS OF THE BAUXITE PROFILE

The color and textural changes were logged through both the Cowlitz and Columbia County cores. The powder density was measured for 9 samples in the Cowlitz County core.

THE COWLITZ COUNTY PROFILE

The core (number 9/1 31 2C) shown in Figure 3, is 7.3 m long and penetrated 1.2 m of an iron pisolite zone over a gibbsite nodular zone. The upper 1.8 m was not included with core samples.

The gibbsite nodular zone is at least 6.1 m thick. The contact against the upper basalt relic zone was not penetrated. The nodular zone contains 0.5 to 4 cm, subrounded, hard, pale brown (5 YR 5/2) (Geological Society of America, 1970), nodules in a moderate reddish brown (10 R 4/6) massive matrix. In the lower portion of this zone the matrix is mottled pale reddish (10 R 5/4) to light brown (5 YR 5/6). The zone has thin platy gibbsite nodules with relic basalt textures separated by moderate reddish brown (10 R 4/6) matrix. The vuggy appearance of the nodules is a relic of the vesicular texture of the basalt (Figure 4a). Well-preserved relic plagioclase microphenocrysts and microlites are visible in thin sections (Figure 4b). The relic felted textures of the primary basalt are destroyed near the edges of nodules in a transitional band to the reddish matrix material.

Figure 3. Cowlitz County core. The core boxes contain the following depths in meters from left to right 8.2 to 9.1, 7.3 to 8.2, 6.4 to 7.3, 5.5 to 6.4, 4.5 to 5.5, 3.6 to 4.5, 2.7 to 3.6, and 1.8 to 2.7 meters.

a.

b.

Figure 4. Relic textures in gibbsite nodules. a. vesicular texture preserved in nodule. b. photomicrograph of relic plagioclase microlites replaced by gibbsite (approximately 1.1 mm across).

The iron pisolite zone contains spherical blackish red (5 R 2/2) to dark reddish brown (10 R 3/4) pisolites that are 2 to 5 mm in diameter in a moderate reddish brown matrix (10 R 4/6). The darker blackish red pisolites are attracted to a magnet. The average diameter of the pisolites is 2 mm. Larger pisolites, which are as large as 3.5 cm, are composites of smaller pisolites of average diameter cemented by iron oxides or oxyhydroxides (Figure 5).

The transition from the pisolite to the gibbsite zone is gradational. Over a thickness of 6 cm the gross color changes subtly and the percentage of iron pisolites increases as the percentage of gibbsite nodules decreases progressing upward through the profile.

THE COLUMBIA COUNTY PROFILE

A core drilled by Reynolds Metals Company in Columbia County, Oregon, to a depth of 7.9 m has an unusually thick, 5.3 m, iron pisolite zone that overlies a 1 m gibbsite nodular zone (Figure 6). The base of the gibbsite nodular zone was not penetrated and this zone is undoubtedly thicker.

The textures and colors in the pisolite zone in this profile are generally the same as the Cowlitz County core. The pisolites are not evenly distributed throughout the profile; the percentage increases with greater depth. Pisolites are less than 1% of the upper 3 m of the core, 5-10% between 3 and 5.5 m, and as much as 50% below 5.5 m. Between 4.9 and 5.5 m, soft grayish orange (10 YR 7/4) patches are surrounded by light brown (5 YR 5/6) matrix. Between 5.5 and 6.4 m, non-magnetic moderate brown (5 YR 4/4) pisolites occur together with the magnetic

Figure 5. Iron pisolites. Note that the larger pisolite is a composite of smaller pisolites.

Figure 6. Columbia County Core. The core boxes contain the following depths in meters from left to right 1.7 to 2.4, 2.4 to 3.4, 3.4 to 4.3, 4.3 to 6.1, 6.1 to 7.0, 7.0 to 7.9, and 7.9 to 8.2 meters.

darker blackish red (5 R 2/2) pisolites that are dominant above. The transition to the gibbsite zone is gradational as the number of pisolites decrease toward the base of the zone.

POWDER DENSITIES

The density was measured on powdered materials from the gibbsite nodular zone, pisolite zone, and a fresh basalt sample. The determination of density on powdered materials minimizes the effect of buoyancy on measurements caused by air trapped in pores. The powder density of selected samples was measured using the method described by Winchell (1938). Isopropanol was substituted for toluene as the organic liquid in the pycnometer ($\rho = .7837$ g/ml). Organic liquids such as toluene, xylene, ethanol, bromoform, and benzene are preferable to water because their characteristic high wetting power and low surface tension lower the tendency to entrap air in the powdered solid. Isopropanol is preferable to most organic solvents because of its low toxicity. To insure that absorbed water in the bauxite was not released into the isopropanol, samples were dried by heating for 2 hours at 150° C. As a comparison, a powder density measurement was repeated using ortho-xylene ($\rho = .8800$ g/ml) as the liquid.

A possible major source of error is the adherence of air bubbles to the surface of the particles. Other sources of error include variation in the pycnometer volume due to temperature variations, and the seating of the stopper. An average powder density was calculated from between 2 and 6 repeat measurements. The standard deviations ranged between .04 and .001 g/ml.

The powder densities measured for the different zones in the Cowlitz County profile show little variation (Table I). The powder density of corestone S-200A is 2.87 g/ml, which is consistent with values reported for basalt in the literature (Daly et al., 1966). The powder density of bauxite ranges between 2.67 to 2.89 g/ml. The bulk samples with the lowest powder density, 2.69 and 2.76 g/ml, are in the upper part of the gibbsite nodular zone.

TABLE I

POWDER DENSITIES FOR THE COWLITZ CO. PROFILE

Sample Number	Depth meters	Zone ²	Powder Density g/ml	# of measurements	Standard Deviation
9/3-2	2.44	Piso.	2.86	4	0.009
9/3-17	2.59	Piso.	2.89	2	0.001
9/3-5	3.35	G.N.	2.76	3	0.002
9/3-8	4.27	G.N.	2.69	3	0.006
9/3-18 ¹	5.33	G.N.	2.83	6	0.01
9/3-10	5.79	G.N.	2.85	4	0.002
9/3-20	6.86	G.N.	2.79	4	0.008
Average	2.81				
Gibbsite nodule separates					
9/3-18A	5.33		2.67	3	0.04
9/3-20A	6.86		2.75	4	0.02
Basalt corestone S200A			2.87	4	0.005

¹9/3-18 Powder density is 2.78 g/ml when measured with ortho-xylene as displacement fluid in pycnometer.

²Piso = Pisolite zone

G.N. = Gibbsite nodular zone

MINERALOGY

The mineral constituents of selected bauxite samples within each zone of the profile were identified using X-ray diffraction (XRD). Mössbauer spectroscopy was used to aid in the identification of iron phases. Five bulk samples selected from the Cowlitz County core were used for determination of the mineralogy through the profile. The mineral identification of pisolites was done on pisolite separates from both the Cowlitz and Columbia County cores.

METHODS

Bulk samples, pisolites (samples 9/3-1B, 5/1-2B and 5/1-2C), and gibbsite nodule separates (samples 9/3-18A and 9/3-20A) were gently ground and sieved to less than A.S.T.M. 200 mesh size for XRD analysis. Powder mounts were prepared by gentle-pressure, back-filling the powdered sample into aluminum sample holders. The holders were placed against a frosted plastic slide to minimize orientation (Moore and Reynolds, 1989). XRD data were collected using $\text{CuK}\alpha$ radiation (45 kV, 18 mA) on a General Electric XRD-5 D/F X-Ray Unit using a MR soller slit, a $.1^\circ$ receiving slit, 1° beam tunnels and a Ni filter. Samples were scanned twice, once at a rate of 4° 2θ /minute with a count rate of 1000 counts/second and a second time at a rate of 2° 2θ /minute with a count rate of 500 counts/second for finer peak resolution. Because of poor peak resolution due to the high fluorescence background caused by

high iron concentration and to the poor crystallinity and small particle size of the iron oxides, semi-quantitative analysis of the mineralogy was not attempted. A Debye-Scherrer, 11.5 cm diameter X-ray powder camera was used for one pisolite sample (5/1-2B) because the sample was too small to analyze by standard methods on the General Electric diffractometer.

Removal of poorly ordered iron oxides by dithionite treatment described by Mehra and Jackson (1960) and removal of the crystalline aluminum components with .5M NaOH treatment as described by Hashimoto and Jackson (1960) were used to aid in identifying the iron and aluminum oxides and oxyhydroxides. The separation treatments were performed on sample 9/3-15 at 4.88 m in the profile in the gibbsite nodular zone. To aid in the identification of goethite two samples were heated for one hour at 330°C for comparison with the diffractograms from untreated samples. The 4.18Å peak for goethite is eliminated by heat treatment as goethite is converted to hematite. Measuring the intensity of the hematite (104) peak (2.69Å) before and after heat treatment (Taylor and Graley, 1967) semi-quantitatively determines the percentage of goethite and hematite. Unfortunately, heat treatment also transforms maghemite to hematite which causes an overestimate of the original hematite content.

Mössbauer spectra were collected at room temperature using a ^{57}Co source in rhodium. Velocity was calibrated using an Fe foil absorber. The spectra were fitted to Lorentzian peaks using a non-linear least squares curve fitting computer program (Don Howard, personal communication).

RESULTS

Both gibbsite and hematite are ubiquitous in the profile. Clay minerals, particularly kaolinite, are absent or at a very low abundance. The (001) peak of kaolinite at $7.15\text{\AA}$ was not observed in any of the samples. Table II summarizes relative abundance of gibbsite, hematite, goethite, maghemite, and quartz through the Cowlitz County profile based on relative intensity of XRD peaks. Figure 7 shows the diffractograms for the samples in Table II.

TABLE II

MINERALOGY OF COWLITZ COUNTY PROFILE
AS DETECTED BY XRD

Sample Number	Depth meters	Zone ¹	Gibbsite	Hematite	Goethite	Maghemite	Quartz
9/3-1	2.13	Piso	XX	XX		XX	XXX
9/3-3	2.74	Piso	XXX	XX	XX	XX	XX
9/3-5	3.35	G.N.	XXXX	XX	XXX		
9/3-15	4.88	G.N.	XXXX	XX	XXX		
9/3-13	7.92	G.N.	XXX	XX	XX		
Relative peak intensity							
XXXX Strong			XXX Medium	XX Weak			

¹Piso = Pisolite zone

G.N. = Gibbsite nodular zone

The intensity of the gibbsite (002) peak at $4.85\text{\AA}$ increases from the top of the core at 2.12 m in the pisolite zone to the middle part of the gibbsite nodular zone at 4.88 m. The decrease in peak intensity for the sample at 7.92 m reflects the decrease in abundance of the more

Figure 7. X-ray diffractogram of bulk samples through Cowlitz County core. G = Gibbsite, Go = goethite, H = hematite, M = maghemite, and Q = quartz.

crystalline gibbsite nodules in the lower part of the core. Samples 9/3-5 and 9/3-15 from the gibbsite nodular zone yield strong peaks at 2.24, 2.17, 2.04, and 1.99Å. These peaks are very weak or absent in samples with poorer crystallinity. Other aluminum hydroxides and oxyhydroxides such as boehmite (γ -AlOOH), diaspore (AlO(OH)), and bayerite (Al(OH)₃) were not detected.

Goethite, hematite, and maghemite (γ -Fe₂O₃) are the iron phases in the profile. The 2.70Å (104) diffraction peak as well as the red color characteristic of the entire core is diagnostic of hematite. The intensity of this (104) peak does not vary significantly through the profile. Goethite is recognized by a broad peak at 4.18Å (110) at the tail of the stronger (110) gibbsite peak at 4.32Å (Figure 8). The broad, low peak in Figure 8 suggests poor crystallinity or very small particle size typically encountered in soil goethite (Schwertmann, 1985). Goethite was not identified in samples from the pisolite zone (Figure 8).

The magnetic nature of iron pisolites in the pisolite zone and a diffraction peak at 2.95Å (220) are characteristic of maghemite. However, such features would also be noted for magnetite. Maghemite (γ -Fe₂O₃) has a composition close to hematite (α -Fe₂O₃) but is distinguished by its high magnetic susceptibility and remanent magnetism. Based on Mössbauer spectroscopy (Figure 9) the ferromagnetic iron concretions are identified as maghemite rather than magnetite. The Mössbauer spectrum of magnetite at room temperature (Figure 9a) shows a characteristic magnetic splitting, the larger peak contributed by the tetrahedral Fe³⁺ and the smaller by the octahedrally-coordinated Fe³⁺ and Fe²⁺. The

Figure 8. Goethite (110) peak in sample 9/3-5 in gibbsite nodular zone. Goethite is not detected in pisolite zone (sample 9/3-1). Note the sharp peak for pure, crystalline goethite. G = gibbsite, and Go = goethite.

Figure 9. Mössbauer spectra of iron pisolites. a. magnetite (Don Howard, Portland State University), b. magnetic pisolite (sample 5/1-2b), c. non-magnetic pisolite (sample 5/1-2c).

pattern in Figure 9b is entirely due to Fe^{3+} ions. The spectra in Figure 9b may be due to the $\alpha\text{-Fe}_2\text{O}_3$ or $\gamma\text{-Fe}_2\text{O}_3$ phases, but together with the XRD data the evidence suggests that pisolite 5/1-2B is composed of maghemite.

Mössbauer spectra for the pisolite separates in Figure 9b and 9c are attributed to two components. The sharp ferromagnetic component is characterized by coarser crystal sizes, and the broad non-magnetic component is due to fine crystals too small to contain ferromagnetic domains. The sharp peaks that distinguish the maghemite pisolites (Figure 9b) are extremely weak in the non-magnetic pisolite which has a strong central peak (Figure 9c). The non-magnetic pisolites are composed of about 80% of the fine-grained component (i.e. small magnetic domains) while the crystalline maghemite pisolites are defined by 99% of the magnetic component.

Quartz occurs only in the pisolite zone (samples 9/3-1 and 9/3-3) and is the only crystalline silicate phase detected.

Diffractograms of the separates of magnetic iron pisolites (Figure 10) show that they are composed of maghemite, hematite, and quartz. The strong crystallinity of the maghemite is indicated by the intense (100) peak and the high reflectance of the pisolites in reflected light (Figure 11a). Transmitted light micrographs (Figure 11b) show that quartz occurs as grains within the pisolites. Abreu et al. (1988) suggest that quartz acts as a nucleation site for maghemite. The non-magnetic pisolites are composed of poorly crystalline goethite and minor gibbsite (Figure 10). Goethite has a broad yet distinct (110) peak.

The gibbsite nodule separates have a very high degree of

Figure 10. X-ray diffractogram of magnetic (sample 9/3-1b) and non-magnetic pisolite (sample 5/1-2c). Go = goethite, H = hematite, M = maghemite, and Q = quartz.

a.

b.

Figure 11. Photomicrograph of pisolite. a. reflected light (photo approximately .5 mm across). b. transmitted light (3.5 mm across).

crystallinity as evidenced by the intensity of even the weakest diffraction peaks (Figure 12) and the blocky fractures in the SEM photomicrograph (Figure 13). Goethite is also present in the nodules.

The SEM photomicrograph (Figure 13) of the gibbsite nodule shows remarkably little porosity development.

Figure 12. X-ray diffractogram of gibbsite nodule (sample 9/3-20a).

2 microns

Figure 13. SEM photomicrograph of the fracture surface of a gibbsite nodule. The bright particles are iron oxides and oxyhydroxides adhering to the surface and collecting a potential in the electron beam. Note the blocky surfaces of the fracture which suggest a high degree of crystallinity.

GEOCHEMISTRY

Geochemical investigation of the bauxite profiles was designed to examine elemental concentration with respect to depth in the profile and fractionation between pisolites and matrix in the iron pisolite zone. The Cowlitz County core and, to a lesser extent, the Columbia County core were examined for geochemical patterns through the profile. Pisolite-matrix fractionation studies were conducted primarily on the Columbia County core.

METHODS

Approximately 200 gm samples were collected at an interval of about 30 to 60 cm through the Cowlitz Co. core in order to examine the vertical geochemical changes in the profile. Where the core was poorly indurated and friable, the sampling interval was 60 cm to reduce the impact due to mixing of samples in core boxes.

Pisolites or gibbsite nodules were hand picked and separated from the surrounding matrix in order to detect fractionation of elements between the matrix and the gibbsite nodules or iron pisolites. Two gibbsite nodules for which relic textures were confirmed in thin sections (samples 9/3-18A and 9/3-20A) were analyzed separately. For two selected core samples in the Columbia County core the magnetic and non-magnetic pisolites were separated with a hand magnet in order to investigate the elemental concentrations in these two types of

pisolites. For each sample, a bulk analysis and as many as three subsamples consisting of matrix material, gibbsite nodules, and pisolites were prepared.

The geochemistry of the profile was examined by instrumental neutron activation analysis (INAA). Samples were irradiated at the Reed College Reactor Facility in Portland, Oregon. The procedure is outlined in Appendix A and the theoretical as well as practical aspects of INAA are covered by Potts (1987). A total of 91 samples were analyzed by INAA, two batches of 39 and a one batch of 13 in the Reed College Reactor.

THE PARENT BASALT

Based on the geologic mapping of Walsh (1987) and geochemical analysis of a basalt corestone done in this study and by Jackson (1974), the ferruginous bauxite profile in Cowlitz, Co. developed from either the Pomona Member of the Saddle Mountains Basalt or the Frenchman Springs Member of the Wanapum Basalt. Walsh mapped the Saddle Mountains Basalt as outcropping on the plateaus and ridge tops in Wahkiakum and Cowlitz counties in SEC. 31, T. 9 N., R. 3 W. The Wanapum Basalt, which is stratigraphically below the Saddle Mountains Basalt is exposed in stream valleys in the same areas. Basalt sample RLJ-2-71, collected by Jackson (1974) along Cathlamet Road in a small rock quarry (NE 1/4, SEC 7, T. 8 N., R. 5 W.), is from the Pomona Member based on the high Cr and low TiO_2 concentration (Swanson and Wright, 1981). Since a fresh basalt sample was not found in the cores used in this study, the parent could be from either of these two flows. Table III summarizes the major,

minor, and trace element geochemistry for these two members.

The starting material for the Columbia County, Oregon, core is the Frenchman Springs Member based on analysis of a basalt corestone S-200A collected by Jackson from a test pit excavated by Reynolds Metals Co. in 1972. The test pit, located 4.5 miles northwest of St. Helens (NW 1/4, SEC 23., T. 5 N., R. 2 W.), is near the site of the Columbia Co. core used in this study.

THE VERTICAL DISTRIBUTION OF ELEMENTS IN THE PROFILE

Groups of elements display similar patterns of behavior in the bauxite profile. The groups are:

1. lanthanide elements (La, Ce, Sm, Eu, Lu) and the alkali metal Na,
2. transition metals of groups 3B through 8B (Sc, Ti, V, Cr, Mn, Fe, Co),
3. high field strength elements (Hf, Ta), semimetals in group 5A (As, Sb), and the actinide elements (Th, U).

In the following section, one element has been selected from each of these three groups to illustrate the geochemical behavior in the profile. Table XIII (Appendix B) and Table XIV (Appendix C) show major, minor, and trace element concentrations through the Cowlitz and Columbia profile respectively.

Distribution of major and trace elements measured in the Cowlitz profile shows three distinct patterns in the gibbsite nodular and iron pisolite zones. The lanthanide elements and Na show a progressive decrease in concentration with increasing depth in the profile. Figure 14, a plot of La concentration versus depth, illustrates this decrease

TABLE III

AVERAGE MAJOR, MINOR AND TRACE ELEMENT CONCENTRATIONS OF THE
POMONA MEMBER OF THE SADDLE MOUNTAINS BASALT AND THE
FRENCHMEN SPRINGS MEMBER OF THE
WANAPUM BASALT

	Pomona ¹	Frenchman ²	Corestone		RLJ-2-71
			S-200A INAA ³	XRF	INAA ³
Oxides in Wt %					
SiO ₂	51.88	52.41		51.9	
Al ₂ O ₃	14.88	13.97		14.22	
Fe ₂ O ₃	11.63	14.48		11.26	
TiO ₂	1.62	2.93		3.08	
MgO	5.94	4.25		3.51	
CaO	10.11	8.51		8.87	
K ₂ O	.64	1.4		1.43	
Na ₂ O	2.36	2.92	2.66	3.00	2.35
P ₂ O ₅	0.34	0.58		0.58	
ppm					
As	NA	NA			
Ba	235	564		535	
Ce	34.5	52.5		45	
Co	43.4	39.4	85.7		41.2
Cr	112	33.1	48.8	51	115.8
Cs	NA	0.95			
Eu	1.43	2.3			
Ga	20			20	
Hf	3.2	4.35	5.41		5.04
La	17	26.5	19.6	20	20.8
Lu	0.39	0.63	0.56	0.29	
Mn	1317	1626		5328	
Sb	NA	NA			
Sc	34.35	36.4	34.4	40	38.4
Sm	4.7	7.2	6.4		3.8
Ta	0.77	1.01			
Th	2.5	3.7	5.89	4	3.41
U	NA	NA			
V	295	422		445	
Yb	2.7	3.4	6.26		
Zn	181	201		137	
Zr	445	232			

¹Average concentration values for Pomona from Swanson and Wright (1981) based on 30 samples.

²Average for Frenchman Springs by Beeson et al. (1989) from 11 samples and for the trace elements from Swanson and Wright (1981) based on 8 samples.

³INAA on corestone S200A and RLJ-2-71 performed by Jackson (1974).

in concentration from 10.6 ppm in the pisolite zone to .74 ppm in the gibbsite nodular zone. The concentrations of As, Sb, Th, Hf, and Ta decrease upward through the pisolite zone and increase upward in the gibbsite nodular zone. Figure 14 shows the concentration of Hf versus depth. The transition metals Fe, Ti, V, and Cr have similar patterns as depth increases in the profile. In the pisolite zone, concentration increases as depth increases, and in the upper part of the gibbsite nodular zone the concentration is constant but lower than in the pisolite zone above. The lower part of the gibbsite nodular zone has more variable concentrations of the transition metals than the upper part of the same zone. This pattern is illustrated in Figure 14 with the plot of Fe_2O_3 versus depth.

In the thick pisolite zone in the Columbia County profile, the elements show the same pattern as in the thinner pisolite zone in the Cowlitz County profile (Figure 15). The same three categories of elements are apparent in the thick pisolite zone.

The groupings of elements into three sets is further supported by statistical correlation and cluster analysis. The correlation coefficient, r , shows the degree of interrelation between a pair of variables. A correlation coefficient of +1 is a perfect direct relationship between two variables. A correlation of -1 is a perfect inverse relationship. Zero is no relationship at all. Based on the t test of correlation (Davis, 1986) and a two-sided significance level of 10%, the critical r value is .482. Any pair of elements with a correlation coefficient greater than .482 or less than -.482 shows a significant statistical relationship at a 10% level of significance.

Figure 14. La, Hf, and Fe₂O₃ concentration versus depth in the Cowlitz County core.

Figure 15. La, Hf, and Fe₂O₃ concentration versus depth in the Columbia County core.

The correlation coefficients for each pair of elements with a significant relationship are shown in the matrix in Table IV. The pairs of elements within the following three groups show a significant relationship: lanthanide elements and Na; the transition metals; high field strength elements, semimetals (As and Sb), and Th. Semimetals also correlate with lanthanide elements. The dendrogram produced by cluster analysis (Davis, 1986) in Figure 16 is constructed from the correlation matrix in Table IV. Pairs of elements with the highest similarity or the largest correlation coefficient, r , cluster together in the dendrogram in Figure 16. With the exception of Ce and Lu, the dendrogram clusters the elements into three families identical to the categories picked by inspection. The dendrogram clusters the following sets of elements:

1. the transition metals of groups 3b through 8b;
2. lanthanides (Sm, Eu, La) and Na;
3. high field strength elements, Th, the semimetals (As, Sb) and Lu.

ELEMENTAL RATIOS

Because of heterogeneous mass and volume changes within the weathering profile, an interpretation of element mobility based on chemical concentrations is misleading. For example, by removing SiO_2 from the parent rock the concentration of Fe is increased even though it may not be mobilized in the profile. If elements are removed or added during the weathering process, the ratio between the immobile components will remain nearly constant through the profile, and the ratio will be the same as in the parent rock. There is always the possibility that

TABLE IV

CORRELATION COEFFICIENT MATRIX OF ELEMENTS IN THE COMLITZ CO. PROFILE

	Na	Al2O3	Sc	TiO2	V	Cr	Mn	Fe2O3	Co	As	Sb	La	Ce	Sm	Eu	Lu	Hf	Ta	Th	U
Na																				
Al2O3	-0.76																			
Sc																				
TiO2																				
V																				
Cr																				
Mn																				
Fe2O3																				
Co																				
As																				
Sb																				
La																				
Ce																				
Sm																				
Eu																				
Lu																				
Hf																				
Ta																				
Th																				
U																				

Critical $r = .482$ at a significance level of 10% r values outside this region are not shown in the matrix.

Figure 16. Dendrogram for similarities among elements in the Cowlitz County core.

two elements have been added in the same ratio that existed in the parent rock. This could happen in the case of two elements with a similar geochemical behavior, such as K and Rb which are mobilized together. When using ratios to establish immobility of a pair of elements relative to the parent rock, it is best to use two elements that are geochemically dissimilar.

Ratios were determined between elements to determine which elements maintained constant or near constant ratios. Various permutations of ratios between elements were performed to isolate the elements that produced the least changes through the profile. Table V contains the elemental ratios for the bauxite core, and ratios for the average compositions for the Frenchman Springs (Sand Hollow Flow) and Pomona Members.

Extensive bauxite deposits form by the removal of silica and the relative enrichment of Al and Fe (Valeton, 1972). A bauxite deposit formed exclusively by the removal of silica will have a relative enrichment of Al and Fe due entirely to volume reduction and removal of mass. Aluminum and Fe are concentrated while remaining immobile. Although the concentration of Fe and Al are greater, the Al/Fe ratio will be the same as the parent rock. The concentrations of Al and Fe in the core are approximately 2 to 3 times that in the parent basalt. The Al/Fe ratio in the profile (Table V) averages 1.5 compared to from .7 to 1.0 for the parent basalt. Therefore, either Al has been enriched or Fe is slightly depleted. Clearly either Al or Fe are mobile during the development of the bauxite.

TABLE V
SELECTED ELEMENTAL RATIOS IN
IN COWLITZ CO. PROFILE

SAMPLE NAME	DEPTH (meters)	Al:Fe	V:Fe	V:Cr	Ta:Hf	Th:Hf
9/3-1	2.13	1.2	32	2.6	0.1	1.2
9/3-16	2.29				0.2	1.2
9/3-2	2.44	1.2	33	2.8	0.2	1.3
9/3-17	2.59	0.9	34	2.6	0.2	1.3
9/3-3	2.74	0.9	38	3.0	0.1	1.3
9/3-4	3.04	2.0	40	2.1	0.1	1.7
9/3-5	3.35	1.5	32	2.0	0.1	1.7
9/3-6	3.66	2.0	41	2.0	0.1	1.6
9/3-7	3.81	1.9	37	2.2	0.1	1.3
9/3-8	4.27	1.9	34	2.2	0.1	1.0
9/3-9	4.88	2.1	41	2.5	0.1	0.9
9/3-18	5.33	1.0	28	2.8	0.2	0.9
9/3-10	5.79	1.3	42	3.3	0.2	0.8
9/3-19	6.25	1.4	33	2.2	0.2	0.8
9/3-20	6.86	1.3	34	2.8	0.2	0.8
9/3-12	7.32	1.6	39	2.6	0.1	0.7
9/3-21	7.62				0.2	0.7
9/3-13	7.92	1.0	34	2.3	0.1	0.8
9/3-22	8.23				0.2	0.8
9/3-14	8.53	1.4	31	2.3	0.2	1.3
9/3-23	9.14				0.2	0.7
Gibbsite Nodule Separates						
9/3-18A	5.33	2.6	39	2.0	0.2	1.2
9/3-20A	6.86	2.4	34	1.9		1.2
Parent basalts						
Pomona		1.0	36	2.6	0.2	0.8
Frenchmen		0.7	42	12.7	0.2	0.9
Average for profile						
Average		1.5	36	2.5	0.2	1.1
Std. Dev.		0.4	4	0.3	0.0	0.3
Average for gibbsite nodular zone 3.04 to 9.14 meters						
Average		1.6	36	2.4	0.2	1.0
Std. Dev.		0.4	4	0.4	0.0	0.4
Average for pisolite zone 2.13 to 2.74 meters						
Average		1.1	34	2.8	0.2	1.3
Std. Dev.		0.1	2	0.2	0.0	0.0

Ratios for Ta:Hf, Th:Hf, V:Fe, and V:Cr are nearly constant through the core. The Th:Hf ratio is different for the upper and lower half of the gibbsite nodular zone and is consistent with fractionation of Th. Ratios of V:Fe and V:Cr, although constant through the profile, may mobilize proportionally because V and Cr can substitute within iron oxides and oxyhydroxides (Schwertmann, 1989). The ratio between Ta and Hf varies little through the profile and displays no systematic trend. The average Ta:Hf ratio of 0.2 is the same as the ratio for both the Frenchmen Springs (Ta:Hf=0.2, n=8) and the Pomona members (Ta:Hf=0.2, n=30). The values for Ti, although promising, are not considered for this study because of the poor replication of the standards (Table XV, Appendix D).

An alternative method to demonstrate the immobility of one element relative to another is to examine their correlation including both the parent and weathered rock compositions. Both Ta and Hf concentrations of the bauxite samples and the two possible parent basalt flows show a strong linear relationship ($r = .872$). The basalt, nodular gibbsite, and pisolite zones plot in distinct groups defined by linear increases in the Hf and Ta concentrations (Figure 17).

Because of its apparent immobility in the profile and known insolubility in most Eh and pH fields (Brookins, 1987), Hf is assumed to be the least mobile element. Like Ti, Zr, and Nb, Hf is soluble only at an extremely low pH of less than 0.2 (Brookins, 1987). The concentration of Hf is used to calculate ratios against other elements to show systematic enrichment and depletion in the profile. Ratios of other elements against the immobile Hf show systematic changes of

Figure 17. Plot of Ta versus Hf in the Cowlitz County core.

enrichment or depletion in the profile that are independent of mass-volume changes. Table VI shows the ratios of selected group of elements against Hf for samples in the bauxite profile and for the parent basalt flows.

The ratios of Al:Hf and transition metals:Hf indicate progressive depletion of these elements through the upper gibbsite nodular and the iron pisolite zones. The plot of Cr versus depth in Figure 18 shows a constant trend in concentration in the pisolite or the gibbsite nodular zone. However, when Cr is normalized with the immobile Hf (Figure 18), the upward fractionation of Cr becomes apparent due to the upward absolute depletion of Cr.

Lanthanum shows a different behavior in the section. The plot of La:Hf versus depth in Figure 19 shows an enrichment of Lanthanum in the pisolite zone (La:Hf = 0.61 to 0.29) relative to the gibbsite nodular zone (La:Hf = 0.08 to 0.26). The ratio in the parent basalt (La:Hf = 5 to 6) when compared with the ratio in the gibbsite nodular zone suggests a profound depletion of Lanthanum. Considering the other ratios of Hf to lanthanide elements (Hf:Eu, Hf:Sm, Hf:Lu) all, with the exception of Ce, show the same pattern of enrichment in the pisolite zone. Arsenic and Sb behave in a similar manner as the lanthanide elements (Table VI). The concentration for As and Sb in the parent basalt is not well constrained.

MASS-VOLUME CHANGES

Where the relic texture of the basalt is preserved, such as in the gibbsite nodules, the assumption is made that the alteration has

TABLE VI

RATIOS OF SELECTED ELEMENTS WITH HAFNIUM IN COWLITZ CO., WA., PROFILE

SAMPLE NAME	DEPTH meters	Na:Hf	Al:Hf	Sc:Hf	V:Hf	Cr:Hf	Fe:Hf	Co:Hf	Ga:Hf	As:Hf	Hf:Sb	La:Hf	Ce:Hf	Hf:Sm	Hf:Eu	Hf:Lu	U:Hf
9/3-1	2.13	9.6	1.0	1.5	27.1	10.3	1.8	0.4	4.2	0.9	10.7	0.6	1.6	9.2	42.7	76.1	0.4
9/3-16	2.29	6.0		1.6		10.0	1.8	0.3		1.2	15.6	0.4	2.3	11.1	67.9	63.5	0.3
9/3-2	2.44	4.5	1.0	1.4	28.9	10.2	1.8	0.3	4.4	0.9	10.9	0.4	2.3	11.7	59.1	91.4	0.4
9/3-17	2.59	3.5	0.8	1.7	29.0	11.2	1.8	0.2		0.9	17.0	0.3	1.9	15.0	57.4	65.9	0.3
9/3-3	2.74	3.2	0.8	1.8	33.4	11.3	1.8	0.2	3.9	1.2	12.4	0.3	1.5	15.8	67.6	95.8	0.3
9/3-4	3.04	3.5	1.7	2.5	35.3	16.7	1.8	0.4	3.9	1.4	17.7	0.1	2.4	19.7	69.0	125.5	0.4
9/3-5	3.35	3.2	2.0	2.9	41.9	20.5	2.6	0.4	4.6	1.3	14.2	0.1	1.3	18.1	74.7	140.0	0.4
9/3-6	3.66	3.5	2.2	3.1	44.0	21.6	2.2	0.6	4.8	1.2	21.5	0.1	3.0	16.8	63.3	114.0	0.4
9/3-7	3.81	4.7	2.4	4.4	45.8	20.7	2.6	0.9	5.2	1.1	18.5	0.1	3.9	13.7	56.5	120.0	0.5
9/3-8	4.27	3.9	2.7	3.8	50.3	23.1	3.0	0.9	5.0	0.5		0.1		15.2	48.9		0.5
9/3-9	4.88	5.4	3.8	6.0	74.1	29.1	3.7	1.2	6.0	0.5		0.1	0.9	11.9	58.3		0.7
9/3-18	5.33	4.4	2.1	7.9	58.4	21.0	4.2	1.5		0.5	15.3	0.2	2.2	10.0	28.1		0.4
9/3-10	5.79	4.6	2.6	7.0	79.2	24.0	3.9	1.3	5.8	0.3		0.1	1.1	16.7	60.0	52.9	0.4
9/3-19	6.25	6.3	2.6	8.6	60.5	27.2	3.8	1.1		0.3	28.7	0.1	1.0	15.6			
9/3-20	6.86	7.1	2.3	8.1	59.3	21.4	3.5	1.3		0.3		0.1	1.6	18.0	40.9		0.3
9/3-12	7.32	5.8	3.3	8.4	77.4	29.4	4.1	1.5	5.4	0.3		0.1	0.6	14.1	55.4		0.4
9/3-21	7.62	5.2	0.0	8.6		25.4	4.0	1.2		0.3		0.1	0.8	14.1			0.3
9/3-13	7.92	5.1	2.0	8.6	67.2	28.7	4.1	1.5	4.9	0.2		0.1		12.8	43.3		
9/3-22	8.23	8.0	0.0	7.7		23.8	3.7	1.1		0.4		0.3	1.7	8.3	23.1		0.3
9/3-14	8.53	14.5	2.7	5.9	62.2	26.6	4.1	1.3	5.9	1.1	13.3	0.9	6.5	3.5	17.0	48.7	
9/3-23	9.14	6.1	0.0	8.0		24.3	3.8	1.5				0.2	0.6	12.8	26.1		0.4
Gibbsite Module Separates																	
9/3-18A	5.33	18.3	4.9	10.6	72.3	36.6	3.8	1.3	4.7	0.2		0.1	3.9	13.6			0.5
9/3-20A	6.86	32.7	4.4	10.9	62.5	32.7	3.8	1.7	5.1	0.3		0.1	7.0	12.6			0.5
Parent Basalts																	
Pomona	5471	2.5	10.7	92.2	35.0	5.2	13.6	6.3				5.3	10.8	0.7	2.2		8.2
Frenchmen	4980	1.7	8.4	97.0	7.6	4.8	9.1	4.6				6.1	12.1	0.6	1.9		6.9

Ratios of Sb, Sm, Eu, and Lu expressed as Hf:element. Al:Hf and Fe:Hf ratios are wt%/ppm.

Figure 18. Cr concentration and Cr:Hf ratio versus depth in the Cowlitz County core.

Figure 19. Ratio La:Hf versus depth in the Cowlitz County core.

taken place with little volume change (Eggleton et al., 1987). Thus, changes in the concentration of elements should be due totally to mass changes and should reflect a simple relation to the concentration of elements in the parent basalt. Table XIII (Appendix B) lists the elemental concentrations in the gibbsite nodules and the surrounding fine-grained matrix material. Table VII contains ratios of the selected elements between the gibbsite nodule and the parent basalt flow. Compared to the Pomona and Frenchman Springs flows, the Hf concentration is enriched. In the matrix, Hf is enriched by a factor of 3 to 6.

TABLE VII

RATIO OF ELEMENTAL CONCENTRATION BETWEEN GIBBSITE
NODULES AND THE POSSIBLE PARENT BASALT

Sample Basalt	Concentration ratio nodule:basalt			
	9/3-18A Pomona	9/3-18A Frenchmen	9/3-20A Pomona	9/3-20A Frenchmen
Al	3.28	3.49	3.27	3.48
Cr	1.7	5.9	1.7	5.9
Fe	1.22	0.98	1.34	1.07
Hf	1.66	1.22	1.84	1.36
Sc	1.65	1.56	1.88	1.78
Ta	1.53	1.17	N.D.	
Th	2.6	1.8	1.9	1.3
Ti	1.38	0.76	1.38	0.76

N.D. - element not detected

The ratio between the powder densities of the gibbsite nodule and the parent basalt (0.93 to 0.96) shows a minimum of between a 4 to 7% difference in powder density.

FRACTIONATION OF ELEMENTS IN IRON PISOLITES

Thirteen sample sets composed of pisolites, matrix around the

pisolites, and bulk materials including pisolites and matrix were analyzed by INAA. The separates of pisolites and matrix exhibit distinct patterns of fractionation. Ratios of elemental concentrations in the pisolites relative to matrix are given in Table VIII. The degree of fractionation between the matrix and pisolites is less pronounced in the lowermost part of the pisolite zone for both the Cowlitz and Columbia county profiles. A meter above the gibbsite nodular zone the ratio for Fe in the Columbia Co. profile decreases from about 5 to between 3.06 and 1.98. The difference in the concentration of iron in the pisolites and the matrix is less, and the matrix and the pisolites are more similar in composition at the lower part of the pisolite zone. This pattern corresponds with an increase in the percentage of non-magnetic goethite pisolites. The pattern is most pronounced for Na, Sm, La, Ga, Cr, and Fe.

Elements more concentrated in the pisolite than the matrix are As, Sb, Ga, Hf, Th, Cr, Sc, Fe, and Ta. Elements more concentrated in the matrix than the pisolites are the lanthanides, Na, and Co. The elements with greater concentration in the pisolites, particularly the transition metals, also decrease in concentration with increasing depth in the pisolite zone. The lanthanides and Na, which have a higher concentration in the matrix, increase in concentration with depth in the pisolite zone.

The ferromagnetic maghemite pisolites and the nonmagnetic goethite pisolites also display patterns of elemental fractionation. Samples 5/1-1 and 5/1-2 in Table IX were collected at 5.79 and 6.40 m respectively in the Columbia County profile. The magnetic pisolites

TABLE VIII
RATIO OF ELEMENTAL CONCENTRATION IN IRON PISOLITES TO MATRIX

SAMPLE	Pisolite:matrix		V	Mn	Sm	La	As	Sb	Ga	Na	U
	DEPTH	Fe2O3 Al2O3									
	Meters										
	Cowlitz Co. Profile										
9/3-1	2.13	4.13	0.52	1.18	0.59	0.43	1.21	1.35	2.00	0.37	0.86
9/3-2	2.29	4.65	0.33	1.18	0.54	0.45	1.45	1.40	2.07	0.48	0.57
9/3-3	2.44	3.87	0.33	1.26	0.91	0.81	1.58	2.36	2.19	0.78	0.90
	Columbia Co. Profile										
5/1-3	2.13	5.66			0.49	0.32	1.65	2.25	3.96	0.19	0.86
5/1-4	2.74	6.38			0.40	0.18	2.09	1.80	3.58	0.14	1.07
5/1-5	3.35	5.71			0.36	0.21	1.45	2.03	3.31	0.10	0.68
5/1-6	3.96	5.56			0.42	0.24	1.89	2.18	2.83	0.16	0.92
5/1-7	4.27	5.42			0.30	0.19	2.20	2.05	3.55	0.11	0.68
5/1-8	4.57	5.89			0.39	0.26	2.31	2.24	3.49	0.14	0.59
5/1-9	5.03	6.29			0.53	0.41	2.72	2.54	2.14	0.25	0.73
5/1-10	5.49	3.06			0.72	0.66	2.10	1.65	1.69	0.41	0.60
5/1-11	6.1	1.98			0.80	0.74	1.59	1.37	1.15	0.66	0.72
5/1-12	6.71	2.52			0.80	0.68	1.58	1.88	1.88	0.46	0.83

TABLE VIII
RATIO OF ELEMENTAL CONCENTRATION IN IRON PISOLITES TO MATRIX
(continued)

SAMPLE	DEPTH Meters	Pisolite:matrix									
		Eu	Hf	Ce	Lu	Th	Cr	Sc	Co	Ta	
		Cowlitz Co. Profile									
9/3-1	2.13	0.87	1.64	0.52	1.04	1.90	2.43	0.97	0.83	1.32	
9/3-2	2.29	0.89	1.36	0.39	1.04	1.44	2.32	0.89	0.85	1.21	
9/3-3	2.44	1.12	1.31	0.32	1.47	1.33	2.00	0.98	1.05	1.46	
		Columbia Co. Profile									
5/1-3	2.13	0.88	2.18	0.21	0.83	2.07	6.18	1.32	0.64	1.52	
5/1-4	2.74	0.89	2.54	0.30	0.74	2.36	3.29	1.51	0.60	1.28	
5/1-5	3.35	0.71	2.05	0.00	0.85	1.98	2.82	0.90	0.57	1.50	
5/1-6	3.96	0.87	2.29	0.34	0.83	2.45	3.35	1.05	0.61	1.36	
5/1-7	4.27	0.63	1.61	0.32	0.69	1.85	2.15	1.15	0.33	1.48	
5/1-8	4.57		1.78	0.52	0.86	2.04	2.57	1.09	0.39	1.67	
5/1-9	5.03		1.66	0.29	0.94	1.84	3.00	1.22	0.57	1.24	
5/1-10	5.49	1.90	1.03	0.00	0.95	1.16	1.81	1.18	0.71	0.77	
5/1-11	6.1		0.97	0.00	0.86	1.02	1.52	1.20	1.09	0.55	
5/1-12	6.71		1.15	0.00	1.14	1.19	1.74	0.93	0.72	1.15	

have distinctly higher concentrations of Fe, Ga, Sb, and Ta; and lower concentrations of Th, Cr, Sc, Co, As, and light to intermediate lanthanide elements.

TABLE IX
FRACTIONATION BETWEEN MAGNETIC AND
NON-MAGNETIC PISOLITES

SAMPLE	5/1-1	5/1-1A	5/1-1B	5/1-1C	5/1-2	5/1-2A	5/1-2B	5/1-2C
	Bulk	Matrix	Piso- lite ¹	Piso- lite ²	Bulk	Matrix	Piso- lite ¹	Piso- lite ²
Oxide in wt%								
Fe ₂ O ₃	35.19	29.26	83.8	42.64	39.71	21.3	80.9	40.94
ppm								
As	27.6	30.4	38.9	42.7	33.3	21.8	37.1	49
Ce	30.3	28.7	7.5	23.2	19.3	32.9	0	9.1
Co	6.2	5.6	3.3	7	4.6	4.4	2.7	5.9
Cr	145	141	179	223	147	101	166	175
Eu	0.32	0.31	0.29	0.36	0.33	0.29	0.29	0.37
Ga	81	74	214	67	124	101	216	85
Hf	22.9	26.4	26.2	26.8	29.1	27	25	29.7
La	3.27	4.48	3.05	3.4	4.68	5.18	2.98	4.6
Lu	0.14	0.1	0.19	0.13	0.21	0.2	0.27	0.11
Na	39.4	48.9	22.4	28.3	39.5	57.4	21.5	35.6
Sb	1.38	1.65	3.64	1.84	2.3	1.84	3.48	2.25
Sc	38.98	37.24	19.29	53.2	29.66	24.74	15.2	43.32
Sm	0.91	1.06	0.82	1.14	1.13	1.23	0.78	1.21
Ta	2.2	2.5	4.7	1.2	4.2	5	5	1.8
Th	30.6	34.6	29.5	37.7	32.7	29.9	25.1	35.5
Yb	0	0.9	1	0	1.3	1	1	0.8

¹5-1b and 5-2b are magnetic pisolites (maghemite)

²5-1c and 5-2c are non-magnetic pisolites (goethite)

DISCUSSION

Since the generation of a saprolite involves replacement of primary mineralogy by minerals stable under surface conditions, changes in mass, volume, and composition are basic to the chemical weathering processes. Relative changes in concentration of an element may take place by removal of other constituents, actual removal by solution, or dilution due to addition of constituents. An increase in the concentration of an element may not reflect mobility of that element in the weathering profile, but may reflect volume changes.

The mobility of elements and changes in mass and volume during weathering has been examined in corestones (Colman, 1982 and Eggleton et al., 1987) and in a profile of weathered volcanogenic sandstone (Duddy, 1980). Assuming Ti as immobile, Colman (1982) calculated a 40-50% volume loss during formation of a weathering rind on andesite corestones. Based on preservation of primary basaltic textures in a corestone, Eggleton et al. (1987) assumed a constant volume and characterized changes in element concentrations as a function of changes in density. The rim of the basalt corestones experienced a 33% mass reduction. Duddy (1980) calculated an 8% volume loss and found that small increases in Al, Si, and Na were due to removal of other elements, particularly Ca, Fe, Mg, Mn, and P.

In order to assess the effects of mass and volume changes on concentration of elements during weathering, the composition of the

parent rock must be known. Although the exact parent flow for the Cowlitz County profile is somewhat uncertain, geologic mapping (Walsh, 1987) and geochemical sampling (Jackson, 1974) narrow the possibilities to the Pomona Member of the Saddle Mountains Basalt and the Frenchman Springs Member (Sand Hollow flow) of the Wanapum Basalt. A comparison of ratios between the generally immobile elements (Ti, Hf, Ta, etc.) in the bauxite and the two possible parent flows allows the most likely parent flow for the bauxite to be determined (Table X). Ratios for the Pomona most closely match the average ratio for the bauxite. For the purpose of modeling mass-volume changes during weathering, the parent basalt flow for the Cowlitz County profile is assumed to be the Pomona.

TABLE X

COMPARISON OF RATIOS OF IMMOBILE ELEMENTS IN BAUXITE
TO POSSIBLE PARENT BASALT FLOWS

Ratio	Average Bauxite ¹	Average Frenchmen	% dif	Average Pomona	% dif
Fe:Ti	8.90	5.8	53.4%	8.4	6.0%
Ti:Ta	1.33	1.74	-23.6%	1.26	5.6%
Th:Hf	1.0	0.9	11.1%	0.8	25.0%
Ta:Hf	0.2	0.23	-13.0%	0.24	-16.7%
Cr:Fe	14	3.3	324.2%	13.8	1.4%
Cr:Ti	132	19	594.7%	115	14.8%
V:Fe	36	42	-14.3%	36	0.0%
V:Ti	315	240	31.3%	304	3.6%
V:Cr	2	12.7	-84.3%	2.6	-23.1%

¹Average ratio for the gibbsite nodular zone

Weathering of the parent basalt to a ferruginous bauxite may take place at constant volume by a change in mass, constant mass by a change in volume, or by a combination of both. If there is minimal change in volume, then reorganization of mass is by element mobility. The best

zone in the profile to examine these relations is in the gibbsite nodular zone. Relic textures in nodules surrounded by fine-grained matrix in these zones is consistent with heterogenous volume changes during the transformation of basalt to bauxite. Within the domain of the gibbsite nodules, volume change is minimal in comparison to the surrounding matrix material where no primary textures are preserved. Considering that a feldspar crystal losses 76% in molar volume during the transformation to gibbsite (Kronberg et al, 1982), preservation of relic plagioclase microlite textures pseudomorphed by gibbsite requires considerable element mobility. The concentration ratio of Al in the gibbsite nodule to Al in basalt (Table VII) suggests that Al is migrating into the domain of the nodule. If the volume of the nodule is conserved, the concentration ratio for immobile elements in the nodule to the parent basalt should be close to 1. The ratios for the most immobile elements, Hf, Ta, Ti, Th, Fe, and Cr, are between 1.3 and 1.9, suggesting a volume decrease in the nodules. However, element mobility or a combination of volume change and mobility cannot be ruled out.

The concentration and volume changes during weathering can be estimated using the concentrations of elements and the density of the parent rock and weathered material. Gresens (1967) derived the following equation for the change in concentration of a single element in A, in this application the basalt, into B, the bauxite:

$$a[f_v(g_b/g_a)c^b - c^a] = x$$

c^a and c^b are the weight fraction of element in the basalt and the bauxite, respectively. The density of the basalt and the bauxite is g_a

and g_b . X is the change in concentration of an element during the transformation of A to B. Because chemical analyses add to 100% by weight, the variable 'a' is often equal to 100 grams. The gains and losses are given in grams per 100 grams. Since there are two unknowns, f_v and x , one of the following two assumptions must be made to solve the equation:

1. The weathering of basalt to bauxite has been at a constant volume, in which case $f_v = 1$ and x for any element can be calculated.
2. One element or a set of elements is immobile ($x = 0$). The volume factor f_v can be calculated and used to solve for the gain or loss of other mobile elements.

For the gibbsite nodules, the assumption of constant volume can be applied to determine the element mobility. The assumption can be tested by assuming that one or a set of elements are immobile and then determining a volume factor. Table XI shows the volume factors assuming element immobility for Al, selected transition metals, and the high field strength elements. The volume factors for the immobile Hf is .57 and .65 for each of the gibbsite nodules. This is an average of a 40% loss in volume. Assuming Fe is immobile, the volume factors are .92 and .85 for each of the nodules. Based on these calculations the assumption of constant volume is not reasonable. A loss in volume could possibly occur as a result of compaction and shrinkage while still preserving textures. Some volume loss may have occurred at the outer surface of the nodule where the relic textures are not preserved.

Volume factors in Table XI for the bulk samples from which the gibbsite nodules were extracted clearly show that most of the volume

reduction takes place in the matrix material surrounding the nodule.

TABLE XI

VOLUME FACTORS ASSUMING ELEMENT IMMOBILITY

SAMPLE DEPTH (% OF ORIGINAL VOLUME)									
NUMBER	meters	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	V	Hf	Th	Cr	Ta
9/3-2	2.44	0.47	0.38	0.44	0.51	0.16	0.10	0.55	0.24
9/3-17	2.59	0.42	0.43	0.39	0.45	0.14	0.08	0.44	0.21
9/3-5	3.35	0.58	0.37	0.73	0.65	0.30	0.14	0.51	0.67
9/3-8	4.27	0.67	0.35	0.72	0.71	0.39	0.31	0.59	0.82
9/3-18	5.33	0.44	0.41	0.51	0.57	0.36	0.31	0.60	0.39
9/3-10	5.79	0.48	0.34	0.47	0.42	0.36	0.34	0.52	0.55
9/3-20	6.86	0.54	0.38	0.55	0.57	0.37	0.37	0.60	0.57
Gibbsite Nodule separates									
9/3-18A	5.33	0.92	0.33	0.78	0.83	0.65	0.41	0.62	0.70
9/3-20A	6.86	0.85	0.32	0.75	0.83	0.57	0.36	0.61	N.D.

For samples 9/3-18 and 9/3-20, the volume loss, based on the immobility of Hf, is approximately 60%, as opposed to 40% in the nodules. The difference in volume loss between the nodule separated from the bulk sample and the bulk sample indicates greater than 60% volume loss in the matrix. The variation in the volume factors also suggests that the volume loss is not evenly distributed in the profile.

Based on estimates for volume loss for each sample, the loss and gains of elements in Table XII clearly show a wholesale absolute depletion of elements in the profile. The relative order of mobility is Na > La > Eu > Sm > Co > Mn > Ce > Sc > Ta > V > Cr > Lu > Th > Fe > Ga > Al. Thorium is the only element that is enriched. Aluminum is both enriched and depleted in samples through the gibbsite nodular zone suggesting that the relatively immobile Al is dissolved and re-precipitated over a small distance. The average absolute depletion in

TABLE XII

ABSOLUTE ELEMENT LOSS BASED ON
IMMOBILITY OF HF

SAMPLE	Depth meters	% gain Na	Al ₂ O ₃	Sc	TiO ₂	V	Cr	Mn	Fe ₂ O ₃
9/3-2	8	-1.00	-0.58	-0.87	-0.64	-0.69	-0.71	-0.97	-0.66
9/3-17	8.5	-1.00	-0.67	-0.84	-0.64	-0.69	-0.68		-0.67
9/3-5	11	-1.00	-0.19	-0.73	-0.59	-0.54	-0.41	-0.98	-0.49
9/3-8	14	-1.00	0.12	-0.64	-0.46	-0.45	-0.34	-0.95	-0.42
9/3-18	17.5	-1.00	-0.13	-0.26	-0.29	-0.37	-0.40	-0.79	-0.19
9/3-10	19	-1.00	0.04	-0.34	-0.24	-0.14	-0.31	-0.84	-0.25
9/3-20	22.5	-1.00	-0.04	-0.23	-0.33	-0.35	-0.38	-0.90	-0.31
Ave. bauxite*		-1.00	-0.04	-0.44	-0.38	-0.37	-0.37	-0.89	-0.33
Ave. pisolite*		-1.00	-0.63	-0.86	-0.64	-0.69	-0.70	-0.97	-0.66
Gibbsite nodule separates									
9/3-18A	17.5	-1.00	0.98	-0.01	-0.16	-0.21	0.05	-0.93	-0.29
9/3-20A	22.5	-0.99	0.78	0.02	-0.24	-0.32	-0.06	-0.93	-0.33

*Average values for the gibbsite nodular zone and the pisolite zone

TABLE XII
ABSOLUTE ELEMENT LOSS BASED ON
IMMOBILITY OF HF
(continued)

SAMPLE	Depth meters	% gain (+) or loss (-)	Co	Ga	La	Ce	Sm	Eu	Lu	Hf	Ta	Th
9/3-2	8	-0.98	-0.98	-0.29	-0.94	-0.79	-0.93	-0.96	-0.91	0.00	-0.34	0.61
9/3-17	8.5	-0.99	-0.99		-0.96	-0.82	-0.94	-0.96	-0.88	-0.01	-0.34	0.67
9/3-5	11	-0.97	-0.97	-0.26	-0.98	-0.88	-0.95	-0.97	-0.94	0.01	-0.55	1.19
9/3-8	14	-0.94	-0.94	-0.20	-0.99		-0.94	-0.95		0.01	-0.53	0.26
9/3-18	17.5	-0.89	-0.89		-0.97	-0.80	-0.92	-0.92	-0.84	-0.00	-0.08	0.18
9/3-10	19	-0.91	-0.91	-0.07	-0.99	-0.90	-0.95	-0.96		0.01	-0.35	0.07
9/3-20	22.5	-0.90	-0.90		-0.98	-0.85	-0.95	-0.94		0.01	-0.35	0.01
Ave. bauxite*		-0.92	-0.92	-0.29	-0.98	-0.86	-0.94	-0.95	-0.89	0.01	-0.37	0.34
Ave. pisolite*		-0.98	-0.98	-0.18	-0.95	-0.81	-0.94	-0.96	-0.89	-0.01	-0.34	0.64
Gibbsite nodule separates												
9/3-18A	17.5	-0.90	-0.90	-0.24	-0.98	-0.64	-0.94			0.00	-0.07	0.57
9/3-20A	22.5	-0.88	-0.88	-0.18	-0.98	-0.35	-0.93			0.01		0.59

*Average values for the gibbsite nodular zone and the pisolite zone

the pisolite zone is greater than in the gibbsite nodular zone for Al, Fe, Cr, V, Sc, Co, and Ga. Ratios of these elements with respect to Hf and the greater absolute depletion of these elements in the pisolite zone compared to the gibbsite nodular zone is consistent with leaching of elements away from the pisolite zone. Re-precipitation may occur lower in the profile.

The concentrations of the lanthanide elements are consistent with mobility within the bauxite profile. Some previous workers (Hanson, 1980, Taylor and McLennon, 1985) believed that the lanthanide elements are immobile during sedimentary processes largely because of the extremely low abundance of lanthanides in most natural waters. This study as well as other studies on weathered profiles (Duddy, 1980; Topp et al., 1984; Schorin and Puchelt, 1987; Banfield and Eggleton, 1989), show that the lanthanide elements are mobilized during the weathering process. Lanthanide elements, with the exception of Ce, remain in solution at pH less than 6 in oxidizing conditions (Brookins, 1987). The lanthanide elements may accumulate in a deeper part of the profile. With more alkaline conditions deeper in the profile, possibly near the weathering front with the fresh basalt, the lanthanide elements may re-precipitate. Gislason and Eugster (1987) recorded a pH between 8 and 9.5 in meteoric spring waters flowing through freshly weathered basalt in Iceland. Under alkaline conditions the lanthanide elements would precipitate from solution. Duddy (1980) found that lanthanide elements and Y accumulate at narrow weathering fronts where they are absorbed by vermiculite clays. Concentration of La + Ce + Nd + Y as high as 10.1 wt% has been recorded in some vermiculite clays. Banfield and Eggleton

(1989) found a similar enrichment in weathered granites.

Despite their similarity in chemical properties, the lanthanide elements are fractionated during the weathering processes. In the Cowlitz profile, Ce is less mobile than other light to intermediate lanthanide elements, possible because of the immobility of Ce in its oxidized Ce^{4+} state (Brookins, 1987). Banfield and Eggleton (1989) found a similar fractionation of Ce in weathered granites. The greater overall mobility of light to intermediate (La, Ce, Sm, Eu) relative to the heavy lanthanide elements (Lu) also suggests fractionation among the lanthanide elements.

In the Cowlitz County profile, alkali metals, Si, and to some extent Fe are leached from the profile leaving Al behind. The residual Al concentrates in the gibbsite nodules, possibly migrating from the surrounding matrix or from higher in the pisolite zone where Al is depleted. The lanthanide elements were probably mobilized during the earlier stages of weathering of the basalt (Duddy, 1980; and Banfield and Eggleton, 1989). The lanthanide elements were released during the breakdown of the unstable glass or the replacement of apatite in the basalt.

The lower volume factors calculated for the immobile Hf in the pisolite zone are consistent with a greater volume reduction in the pisolite zone than the gibbsite nodular zone (Table XI). Volume reduction is accompanied by destruction of primary textures and fractionation of elements between iron pisolites and matrix. Nahon (1987) characterized formation of pisolitic textures in iron crusts as small-scale mobilization of iron between pores with alternating reducing

and oxidizing conditions. Taylor and Schwertmann (1974) showed that slow oxidation rates, higher temperatures (20-40°C), higher pH values (pH 6-8), and high concentrations of Fe^{3+} favor the formation of maghemite rather than lepidocrocite.

In the upper part of the profile goethite disappears, and hematite and maghemite are the dominant iron phases. The process of dehydration, dissolution, and recrystallization of goethite under acidic conditions (pH less than 6) in the pisolite zone may be the process by which trace elements are released into solution and then leached from the upper portion of the profile. Iron oxide and oxyhydroxide minerals substitute Cr, V, Al, Co, Ti, Ga and Mn into the crystal structure (Schwertmann, 1989). As the transition metals are leached from the pisolite zone, primarily from the matrix, the pisolites retain Fe, Cr, and Ga during their growth. Under the same conditions the transition metals that are retained by adsorption by the iron oxides and oxyhydroxides are also released into solution (Evans, 1989). The retention of metals adsorbed on goethite is a function of pH. Typically at lower pH the adsorbed metals are released. Microorganisms or chelation-solutions can dissolve the normally insoluble iron oxides. Elements of low solubility such as Al and Th can be mobilized by dissolved organic acids or ligands (Langmuir and Herman, 1980; Singer and Huag, 1990). Organic ligands may also account for the mobility of such elements as Fe, Hf, Ti, Th, Cr etc. in the weathering profile.

Bauxite deposits developed on recent volcanics in the Tatun volcanic field in Taiwan (Chen et al., 1988) form in aquifers through which water flows from plateaus to lower elevations. Extremely high

rainfall is a requirement for bauxite genesis. In both Taiwan and Hawaii, where bauxite is forming on recent volcanic deposits, the annual rainfall is in excess of 3000 mm with no seasonal variation. Gibbsite along with iron oxides and oxyhydroxides can directly replace the fresh parent rock given such very high water to rock ratios. Pisolites do not occur in the Taiwan profile.

Formation of iron pisolites is favored by a climate with a long dry season. Wetter climates do not permit the development of the alternating reduced and oxidized conditions between pore spaces necessary to develop the pisolitic texture. In the Senegal Basin of West Africa, iron crusts with pisolitic textures are forming where the annual rainfall is between 600 and 1000 mm (Nahon, 1987). This climate is intermediate between the drier Sudanese climatic zone and the humid equatorial zone.

In the Pacific Northwest formation of the pisolite zone over the bauxite represents a change in climate conditions from a continuously wet climate during the formation of the bauxite to a seasonal wet and dry climate during the formation of the pisolites. The further volume reduction, absolute depletion of the relatively immobile transition metals, and the complete destruction of relict textures in the pisolite zone attests to the extreme weathering conditions in the pisolite zone.

Laterization occurred after the extrusion of the Pomona Member at 12 Ma in the middle Miocene and before the deposition of the Portland Hills Silt during the Pleistocene. Flora evidence suggests that the climate during the middle Miocene had extended dry and wet seasons much like the present Pacific Northwest (Wolfe, 1981). The climate during

the Pliocene is not well constrained by fossil plants. Deep saprolite development on younger formations such as the Sandy River Mudstone (Baldwin, 1981), and the Troutdale (Tolan and Beeson, 1984) suggest that the bauxite formed during the Pliocene.

Bauxites in the Pacific Northwest formed within aquifers of extremely high water flow. The formation of the gibbsite nodular zone in the Cowlitz and Columbia County profiles requires permeable surface material. Lateral flow through the nodular and fine-grained gibbsite zones may be focused by the relatively impermeable clay-rich relic basalt zone below. Rainwater percolates into the aquifer and flows to lower slopes. This simple model is based on similar models proposed by Kronberg et al. (1982) and Chen et al. (1988).

The thickest bauxite develops on the narrow spur ridges downslope from higher ridges (Hook, 1976). The greater thickness on the lower ridges is due to greater lateral water flow. The pisolite zone is thickest in the same lower ridges. With the change from continuous year round to seasonal rainfall, the water table experiences greater fluctuations in depth, and the vadose zone undergoes longer periods of drying. The pisolite zone is thickest, as with the Columbia County profile, where the water table experiences greater fluctuations.

CONCLUSIONS

1. Hafnium and Ta are immobile throughout the bauxite profile. The enrichment of Hf and Ta, particularly in the pisolite zone is strictly due to mass-volume changes in the profile and not to element mobility.

2. When compared with Hf, the transition metals and Al show a progressive depletion through the pisolite zone possibly due to leaching in the upper portion of the profile. Re-precipitation probably occurs in the gibbsite nodular zone below. The lanthanides (excluding Ce), As, and Sb are enriched in the pisolite zone relative to the gibbsite nodular zone.

3. When mass-volume changes are taken into account to compute the absolute enrichment or depletion relative to the parent basalt, the alkali metals (Na), lanthanide elements (La, Ce, Sm, Eu, Lu), transition metals (Co, Sc, Fe, Cr, V and Mn), Al, and Ga are depleted while only Th is enriched. The lanthanide elements are probably enriched lower in the profile near the weathering front. Cerium is less mobile than the other light to intermediate lanthanide elements possibly because of its greater immobility in the Ce^{4+} state. Aluminum is both enriched and depleted at different levels in the gibbsite nodular zone suggesting that the relatively immobile Al is mobilized over a short distance possibly from the matrix or the pisolite zone to the gibbsite nodules which are strongly enriched in Al.

4. Assuming the immobility of Hf, the pisolite zone experienced a greater volume reduction (85%) compared to the gibbsite nodular zone (60%). The volume reduction in the pisolite zone is accompanied by the destruction of relic textures and the formation of iron pisolites.

5. The volume change in the gibbsite nodular zone is heterogeneous with greater volume reduction occurring in the matrix material than the gibbsite nodule where relic textures are preserved.

6. Iron pisolites have a greater affinity for As, Sb, Ga, Hf, Th, Cr, Fe, and Ta than the surrounding matrix material. Maghemite pisolites have a greater abundance of Fe, Ga, Sb, and Ta compared with non-magnetic goethite pisolites. During the process of pisolite formation even the most immobile elements experience some small scale mobility. The formation of the pisolite zone above the bauxite represents a change to a drier, seasonal climate from a climate with heavy year round rainfall.

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APPENDIX A

INAA METHODS

The samples were crushed by hand using a hard-steel mortar and pestle. In order to insure uniform particle size of the sample material, the crushed rock powder was sieved through a A.S.T.M. 20 mesh sieve, and the coarse material was crushed again. Approximately one gram sample split was encapsulated in a clean 2 ml (.5 dram) plastic vial and heat sealed. Although a sample with a sufficient weight is important, equivalent volume of all samples including the standards was attained to cancel the affect of differing geometries with respect to the gamma ray detector. The smaller sample vial was placed in a larger vial (8 ml, 2 dram) for irradiation. The samples were irradiated for one hour at 250 kw with a flux of 2×10^{12} neutrons/cm²*sec at the Reed Reactor Facility, Reed College, Portland, Oregon. The reactor is a TRIGA Mark I nuclear reactor. To insure a constant neutron flux, the samples were rotated in a 'lazy susan' in the reactor core. The samples were counted with a coaxial GeLi detector three times after irradiation; 4 to 5 days, 14 days, and 3 months. The U.S.G.S. standards GSP-1 (granodiorite), BHVO-1 (basalt), and Bureau of Standards SRM1633A Coal Flyash were used as standards along with in-house standards BQM (Butte Quartz Monzonite), and PSUCRB-1 (Columbia River Basalt). The measured and the published values for the standards are given in Table XV (Appendix D). The average values for the BQM standard were calculated from analysis done on 11 sample splits in Table XVI (Appendix E).

In order to analyze for elements whose activation products have short half lives, the samples were irradiated for 5 minutes at 5 kw and extracted from the reactor by a pneumatic transfer system for immediate analysis. This method is known as a "rabbit" run. The samples were

counted 15 minutes after irradiation for Al, Ti, Mg, and V, and at 2 hours after irradiation for Dy and Mn. A copper wire of known weight was included with the sample to measure the differences in neutron flux during the irradiation of the sample and the standard. The calculated abundance of the unknown was multiplied by the ratio of Cu activity for the unknown and the standard to correct for the reactor flux changes. Because of poor counting statistics and standard replication, Mg and Dy are not reported.

APPENDIX B

TABLE XIII

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE

SEC 31, T. 9 N., R. 3 W.

TABLE XIII.

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
SEC 31, T. 9 N., R. 3 W.

SAMPLE NUMBER	DEPTH Meters	Al ₂ O ₃ Wt%	Error	TiO ₂	Error	As ppm	Error	Ce	Error	Co	Error
9/3-1	2.13	34.05	0.28	21.55	0.11	2.92	0.18	16.3	0.3	28.1	1.3
9/3-16	2.29			24.15	0.22			22.7	0.9	45	1.3
9/3-2	2.44	38.99	0.32	24.92	0.12	3.7	0.22	17.4	0.3	46.1	1.6
9/3-17	2.59	34.34	0.3	27.53	0.25	4.17	0.31	19.7	0.7	43.3	1.3
9/3-3	2.74	33.57	0.28	28.84	0.14	3.72	0.22	26.7	0.3	34.9	1.6
9/3-4	3.04	45.34	0.36	17.59	0.1	2.21	0.15	18.9	0.3	33.2	1.5
9/3-5	3.35	41.78	0.35	20.69	0.1	2.32	0.19	14.7	0.3	14.5	1.2
9/3-6	3.66	47.17	0.37	17.42	0.09	2.98	0.19	13.7	0.3	34.1	1.4
9/3-7	3.81	44.03	0.37	17.19	0.1	2.81	0.22	10.3	0.3	37.9	1.6
9/3-8	4.27	45.4	0.5	18.5	0.09	2.4	0.17	4.8	0.2	N.D.	
9/3-9	4.88	49.85	0.55	18.31	0.11	2.31	0.17	3.2	0.2	6.4	1.3
9/3-18	5.33	36.45	0.3	26.52	0.26	3.22	0.25	4.5	0.8	19.6	1.6
9/3-10	5.79	43.44	0.49	24.38	0.12	3.44	0.24	3	0.3	9.8	1.5
9/3-19	6.25	41.46	0.35	22.86	0.23	3.29	0.25	2.6	0.6	8.4	1.5
9/3-20	6.86	39.79	0.36	22.32	0.22	3.02	0.24	2.8	0.6	14.3	1.4
9/3-12	7.32	44.24	0.49	20.66	0.1	2.72	0.19	1.8	0.2	4.6	1.4
9/3-21	7.62			29.93	0.3			2.9	0.8	8.2	1.9
9/3-13	7.92	38.64	0.45	29.52	0.15	3.73	0.25	2.2	0.3	N.D.	
9/3-22	8.23			25.3	0.25			4.3	0.7	16.1	1.5
9/3-14	8.53	37.5	0.33	20.68	0.1	2.25	0.19	8	0.2	47.1	1.5
9/3-23	9.14			22.96	0.26			N.D.		5.5	1.4

N.D. = not detected

TABLE XIII.

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
SEC 31, T. 9 N., R. 3 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Cr ppm	Error	Cs	Error	Eu	Error	Ga	Error	Hf	Error	K	Error
9/3-1	2.13	181	3	2.59	0.19	0.41	0.02	74	7	17.5	0.6	1650	70
9/3-16	2.29	197	8	1.68	0.17	0.29	0.02			19.7	0.4	N.D.	
9/3-2	2.44	205	3	1.4	0.2	0.34	0.02	89	8	20.1	0.7	550	50
9/3-17	2.59	251	9	0.96	0.14	0.39	0.03			22.4	0.4	N.D.	
9/3-3	2.74	260	4	1.2	0.2	0.34	0.03	90	8	23	0.8	400	40
9/3-4	3.04	230	3	N.D.		0.2	0.02	54	5	13.8	0.5	130	30
9/3-5	3.35	230	3	N.D.		0.15	0.02	51	5	11.2	0.5	N.D.	
9/3-6	3.66	246	4	N.D.		0.18	0.02	55	5	11.4	0.4	N.D.	
9/3-7	3.81	199	3	N.D.		0.17	0.03	50	6	9.6	0.4	160	40
9/3-8	4.27	203	3	N.D.		0.18	0.02	44	5	8.8	0.4	N.D.	
9/3-9	4.88	204	4	N.D.		0.12	0.02	42	5	7	0.4	N.D.	
9/3-18	5.33	189	9	N.D.		0.32	0.05			9	0.4	N.D.	
9/3-10	5.79	216	4	N.D.		0.15	0.03	52	6	9	0.4	N.D.	
9/3-19	6.25	234	10	N.D.		N.D.				8.6	0.4	N.D.	
9/3-20	6.86	193	9	N.D.		0.22	0.03			9	0.4	N.D.	
9/3-12	7.32	212	4	N.D.		0.13	0.03	39	5	7.2	0.4	N.D.	
9/3-21	7.62	272	31	N.D.		N.D.				10.7	0.5	N.D.	
9/3-13	7.92	298	5	N.D.		0.24	0.06	51	5	10.4	0.5	N.D.	
9/3-22	8.23	231	10	N.D.		0.42	0.05			9.7	0.4	N.D.	
9/3-14	8.53	194	3	1.1	0.4	0.43	0.04	43	4	7.3	0.3	460	40
9/3-23	9.14	209	10	N.D.		0.33	0.06			8.6	0.4	N.D.	

N.D. = not detected

TABLE XIII.

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
SEC 31, T. 9 N., R. 3 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	La ppm	Error	Lu	Error	Mn	Error	Na	Error	Sb	Error	Sc	Error
9/3-1	2.13	10.6	0.17	0.23	0.02	206		4	167.5	1.7	1.63	0.12	25.47
9/3-16	2.29	8.45	0.17	0.31	0.08				118.4	8.4	1.26	0.13	32.42
9/3-2	2.44	8.16	0.15	0.22	0.03	211		4	90.3	1.3	1.84	0.13	27.36
9/3-17	2.59	6.39	0.16	0.34	0.09				79	4.9	1.32	0.13	38.86
9/3-3	2.74	6.61	0.13	0.24	0.03	138		3	73.1	1.2	1.85	0.14	42.06
9/3-4	3.04	1.75	0.07	0.11	0.03	87		2	48.4	1	0.78	0.11	33.81
9/3-5	3.35	1.19	0.06	0.08	0.03	95		5	35.6	0.8	0.79	0.1	32.49
9/3-6	3.66	1.15	0.06	0.1	0.03	203		4	39.7	0.9	0.53	0.11	35.68
9/3-7	3.81	1.32	0.07	0.08	0.03	197		10	45.4	1	0.52	0.12	42.63
9/3-8	4.27	0.75	0.05	N.D.		191		4	34.6	0.8	N.D.		33.64
9/3-9	4.88	0.74	0.05	N.D.		286		5	38	0.9	N.D.		42.25
9/3-18	5.33	1.57	0.1	N.D.		781		33	39.8	4.7	0.59	0.17	71.26
9/3-10	5.79	0.74	0.05	0.17	0.04	574		10	41.6	0.9	N.D.		63.4
9/3-19	6.25	0.86	0.09	N.D.		258		12	54.3	4.1	0.3	0.14	74.32
9/3-20	6.86	1.23	0.1	N.D.		365		16	64	4.7	N.D.		73.1
9/3-12	7.32	0.76	0.05	N.D.		286		5	41.6	0.9	N.D.		60.74
9/3-21	7.62	1.26	0.12	N.D.					55.4	5.4	N.D.		92.34
9/3-13	7.92	1.39	0.08	N.D.		416		7	52.7	1.3	N.D.		89.5
9/3-22	8.23	2.57	0.14	N.D.					77.8	5.7	N.D.		74.37
9/3-14	8.53	6.41	0.13	0.15	0.03				105.5	1.4	0.55	0.09	43.12
9/3-23	9.14	1.67	0.11	N.D.					52.1	5	N.D.		69.15

N.D. = not detected

TABLE XIII.

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
SEC 31, T. 9 N., R. 3 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Sm	Error	Ta	Error	Th	Error	U	Error	V	Error	W	Error
9/3-1	2.13	1.9	0.02	2.3	0.3	21.1	0.2	6.3	0.5	475	15	1	0.11
9/3-16	2.29	1.78	0.03	3.5	0.3	24.6	0.3	6	0.5				
9/3-2	2.44	1.72	0.02	3.2	0.3	25.3	0.3	7.8	0.5	581	17	1.19	0.12
9/3-17	2.59	1.49	0.03	3.6	0.3	29.6	0.3	6.2	0.5	650	18		
9/3-3	2.74	1.46	0.02	2.9	0.3	30.1	0.4	7	0.5	769	21	1.05	0.12
9/3-4	3.04	0.7	0.02	1.25	0.18	24	0.3	5.4	0.4	487	15	0.57	0.09
9/3-5	3.35	0.62	0.02	1.19	0.17	19	0.2	5	0.4	469	14	0.36	0.08
9/3-6	3.66	0.68	0.02	1.4	0.2	18.1	0.3	4.8	0.4	502	16	0.3	0.08
9/3-7	3.81	0.7	0.02	1.27	0.19	12.2	0.2	4.4	0.4	440	14	0.28	0.09
9/3-8	4.27	0.58	0.02	1	0.16	8.65	0.19	4	0.3	443	16	0.21	0.08
9/3-9	4.88	0.59	0.02	0.95	0.17	6.2	0.2	4.7	0.4	519	18	N.D.	
9/3-18	5.33	0.9	0.03	2	0.3	8.3	0.3	4	0.4	526	15	N.D.	
9/3-10	5.79	0.54	0.02	1.4	0.2	7.5	0.2	3.4	0.4	713	23	0.3	0.11
9/3-19	6.25	0.55	0.02	1.5	0.14	6.8	0.3	N.D.		520	16	N.D.	
9/3-20	6.86	0.5	0.02	1.4	0.13	7	0.3	3	0.3	534	16	N.D.	
9/3-12	7.32	0.51	0.02	1	0.2	5.3	0.2	3	0.4	557	18	N.D.	
9/3-21	7.62	0.76	0.03	2.4	0.4	7.7	0.3	3.3	0.4			N.D.	
9/3-13	7.92	0.81	0.03	1.3	0.3	7.8	0.3	N.D.		699	23	N.D.	
9/3-22	8.23	1.17	0.03	1.5	0.15	7.9	0.3	3.1	0.3			N.D.	
9/3-14	8.53	2.09	0.02	1.16	0.17	9.21	0.19	N.D.		454	14	N.D.	
9/3-23	9.14	0.67	0.03	1.9	0.3	5.6	0.3	3.4	0.7			N.D.	

N.D. = not detected

The abundance of Tungsten is calculated relative to sample 9/3-1.

TABLE XIII.

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
 SEC 31, T. 9 N., R. 3 W.
 (continued)

SAMPLE NUMBER	DEPTH Meters	Yb	Error
9/3-1	2.13	1.8	0.3
9/3-16	2.29	1.4	0.2
9/3-2	2.44	1.8	0.3
9/3-17	2.59	1.5	0.3
9/3-3	2.74	1.4	0.3
9/3-4	3.04	N.D.	
9/3-5	3.35	N.D.	
9/3-6	3.66	N.D.	
9/3-7	3.81	N.D.	
9/3-8	4.27	N.D.	
9/3-9	4.88	N.D.	
9/3-18	5.33	N.D.	
9/3-10	5.79	N.D.	
9/3-19	6.25	N.D.	
9/3-20	6.86	1.2	0.29
9/3-12	7.32	N.D.	
9/3-21	7.62	N.D.	
9/3-13	7.92	N.D.	
9/3-22	8.23	1.1	0.4
9/3-14	8.53	0.8	0.2
9/3-23	9.14	0.8	0.3

N.D. = not detected

TABLE XIII.

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
SEC 31, T. 9 N., R. 3 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Al3O3 Wt%	Error	Fe2O3	Error	TiO2	Error	As ppm	Ce	Error	Co	Error
Matrix separate												
9/3-1A	2.13	35.8	0.3	14.15	0.08	3.29	0.25	14	0.3	29.8	1.3	6.5
9/3-2A	2.44	42.06	0.33	15.36	0.09	3.57	0.21	16.6	0.3	55.5	1.6	5.37
9/3-3A	2.74	42.71	0.35	21.37	0.11	4.4	0.26	20.8	0.3	47.5	1.5	4.11
9/3-4A	3.04	41.59	0.33	19.51	0.1	3.58	0.22	19.6	0.3	70.6	1.9	3.91
9/3-5A	3.35			19.28	0.1			14.8	0.3	37.1	1.5	4.23
9/3-6A	3.66	41.53	0.34	20.03	0.1	3.32	0.25	13.5	0.3	43.7	1.5	6.8
9/3-7A	3.81	43.75	0.36	20.71	0.1	2.78	0.22	12.8	0.3	68.1	1.9	7.1
Iron Pisolite separates												
9/3-1B	2.13	18.57	0.18	58.4	0.2	3.87	0.28	17	0.3	15.4	1.4	5.37
9/3-2B	2.44	13.73	0.14	71.4	0.3	4.2	0.31	24	0.3	21.7	1.6	4.57
9/3-3B	2.74	13.97	0.23	82.7	0.4	5.53	0.42	32.8	0.6	15	3	4.3
Gibbsite nodule separates												
9/3-3C	2.74	54.51	0.41	9.47	0.06	0.73	0.09	8.79	0.19	10.5	0.9	1.71
9/3-4C	3.04	49.58	0.39	12.98	0.08	1.75	0.13	11.6	0.2	12.2	1.2	4.81
9/3-5C	3.35			18.18	0.09			12.7	0.2	9	1.1	4.94
9/3-6C	3.66	49.29	0.54	16.69	0.1	2.26	0.16	10.4	0.2	15.6	1.3	8.2
9/3-7C	3.81			16.34	0.1			9.5	0.3	30.9	1.5	7.4
9/3-18A	5.33	48.79	0.47	14.15	0.55	2.24	0.19	1.04	0.2	20.6	0.7	7
9/3-20A	6.86	48.61	0.43	15.55	0.66	2.24	0.2	1.87	0.3	41.2	1.3	9.9

N.D. = not detected

TABLE XIII.

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
SEC 31, T. 9 N., R. 3 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Cr ppm	Error	Cs	Error	Eu	Error	Ga	Error	Hf	Error	K	Error
Matrix separate													
9/3-1A	2.13	147	3	2.3	0.2	0.39	0.02	64	6	16.7	0.6	1560	70
9/3-2A	2.44	171	3	1.6	0.19	0.35	0.03	74	7	19.5	0.7	580	50
9/3-3A	2.74	236	3	0.8	0.3	0.26	0.02	75	7	22.2	0.8	350	40
9/3-4A	3.04	229	3	1.5	0.4	0.3	0.02	84	8	20.3	0.7	210	40
9/3-5A	3.35	231	3	N.D.		0.22	0.02	68	6	14.9	0.5	N.D.	
9/3-6A	3.66	266	4	N.D.		0.22	0.02	58	6	13.4	0.5	N.D.	
9/3-7A	3.81	214	4	N.D.		0.26	0.02	67	7	11.7	0.5	160	40
Iron Pisolite separates													
9/3-1B	2.13	357	5	1	0.3	0.34	0.02	128	11	27.4	0.9	240	30
9/3-2B	2.44	396	5	0.9	0.3	0.31	0.03	153	14	26.6	0.9	N.D.	
9/3-3B	2.74	471	7	N.D.		0.29	0.05	164	15	29	1	N.D.	
Gibbsite nodule separates													
9/3-3C	2.74	115	2	N.D.		0.09	0.02	23	3	7	0.3	N.D.	
9/3-4C	3.04	200	3	N.D.		0.13	0.02	35	4	8	0.3	N.D.	
9/3-5C	3.35	207	3	N.D.		0.15	0.06	36	4	8.5	0.4	N.D.	
9/3-6C	3.66	222	4	N.D.		0.14	0.02	34	4	8.9	0.4	N.D.	
9/3-7C	3.81	190	3	N.D.		0.16	0.02	38	4	7.6	0.4	N.D.	
9/3-18A	5.33	194	1	N.D.		N.D.		25	2	5.3	0.25	N.D.	
9/3-20A	6.86	193	3	N.D.		N.D.		30	3	5.9	0.38	N.D.	

N.D. = not detected

TABLE XIII.
ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
SEC 31, T. 9 N., R. 3 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	La ppm	Error	Lu	Error	Mn	Error	Na	Error	Sb	Error	Sc ppm	Error
Matrix separate													
9/3-1A	2.13	10.36	0.17	0.23	0.02	265		1 170.1	1.8	1.44	0.12	27.01	0.1
9/3-2A	2.44	9.01	0.16	0.26	0.03	198		4 100.3	1.4	1.66	0.12	27.48	0.1
9/3-3A	2.74	4.97	0.11	0.15	0.04	138		3 74.1	1.1	1.48	0.12	31.78	0.11
9/3-4A	3.04	4.39	0.11	0.14	0.03	84		2 70	1.1	1.4	0.12	33.74	0.12
9/3-5A	3.35	2.33	0.08	N.D.				54	1	1.06	0.11	31.8	0.11
9/3-6A	3.66	1.71	0.07	0.12	0.03	241		1 55.6	1	0.74	0.11	38.33	0.11
9/3-7A	3.81	2.87	0.09	N.D.		312		1 64.7	1.2	0.82	0.12	38.56	0.14
Iron Pisolite separates													
9/3-1B	2.13	4.41	0.1	0.24	0.03	316		1 62.5	0.9	1.94	0.13	26.11	0.09
9/3-2B	2.44	4.06	0.1	0.27	0.04	313		1 48.4	0.9	2.32	0.14	24.51	0.09
9/3-3B	2.74	4.05	0.17	0.22	0.06	260		2 57.7	1.6	3.5	0.3	31.28	0.17
Gibbsite nodule separates													
9/3-3C	2.74	0.91	0.05	0.07	0.02	42		1 41.9	0.8	0.33	0.08	19.47	0.07
9/3-4C	3.04	0.81	0.05	N.D.		114		2 42.3	0.9	0.44	0.1	27.71	0.1
9/3-5C	3.35	0.68	0.04	N.D.				36.5	0.8	0.66	0.09	30.18	0.11
9/3-6C	3.66	0.47	0.04	N.D.		249		4 35	0.8	0.26	0.1	39.22	0.14
9/3-7C	3.81	0.67	0.05	N.D.				40.5	0.9	0.37	0.11	41.53	0.12
9/3-18A	5.33	0.63	0.04	N.D.		146		9 97	1.9	N.D.		55.97	0.22
9/3-20A	6.86	0.76	0.07	N.D.		176		10 192.8	3.5	N.D.		64.36	0.29

N.D. = not detected

TABLE XIII.

ELEMENTAL CONCENTRATIONS IN THE COWLITZ COUNTY CORE
SEC 31, T. 9 N., R. 3 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Sm	Error	Ta	Error	Th	Error	U	Error	V	Error	W	Error
Matrix separate													
9/3-1A	2.13	1.84	0.03	2.5	0.3	19.6	0.2	6.4	0.5	433	17	1	0.12
9/3-2A	2.44	1.88	0.02	2.8	0.3	23.3	0.3	8.2	0.5	488	15	1.28	0.16
9/3-3A	2.74	1.13	0.02	2.8	0.3	30.7	0.4	5.8	0.4	770	22	1.05	0.12
9/3-4A	3.04	1.12	0.02	3.4	0.3	33	0.3	6.8	0.5	538	16	1.02	0.15
9/3-5A	3.35	0.76	0.02	1.9	0.2	26.3	0.3	5.9	0.4			0.61	0.1
9/3-6A	3.66	0.75	0.02	1.5	0.2	20.4	0.3	5.4	0.4	574	21	0.34	0.09
9/3-7A	3.81	0.96	0.02	1.2	0.2	17.8	0.3	4.9	0.5	525	20	0.59	0.11
Iron Pisolite separates													
9/3-1B	2.13	1.09	0.02	3.3	0.3	37.3	0.3	5.5	0.4	710	24	1	0.13
9/3-2B	2.44	1.02	0.03	3.4	0.4	33.5	0.4	4.7	0.4	1150	37	1.36	0.17
9/3-3B	2.74	1.03	0.03	4.1	0.6	40.8	0.5	5.2	0.7	1437	49	1.7	0.3
Gibbsite nodule separates													
9/3-3C	2.74	0.3	0.01	0.58	0.11	10.69	0.17	2.5	0.3	235	10	0.24	0.07
9/3-4C	3.04	0.52	0.01	0.81	0.14	10.42	0.19	4.7	0.4	356	13	0.27	0.09
9/3-5C	3.35	0.49	0.01	0.73	0.14	13.1	0.2	4.2	0.3			N.D.	
9/3-6C	3.66	0.52	0.02	1.12	0.17	10.8	0.2	4	0.3	464	16	0.36	0.1
9/3-7C	3.81	0.58	0.02	1	0.16	9.3	0.2	4.1	0.4			N.D.	
9/3-18A	5.33	0.39	0.02	1.18	0.15	6.5	0.24	2.5	0.1	383	14	N.D.	
9/3-20A	6.86	0.47	0.02	N.D.		7.3	0.35	3	0.2	369	13	N.D.	

N.D. = not detected

The abundance of Tungsten is calculated relative to sample 9/3-1A

APPENDIX C

TABLE XIV

ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE

SEC 19, T. 5 N., R. 1 W.

TABLE XIV.

ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE
SEC 19, T. 5 N., R 1 W.

SAMPLE NUMBER	DEPTH Meters	Fe2O3 W%	Error	As ppm	Error	Ba	Error	Ce	Error	Co	Error	Cr	Error
5/1-3	2.13	13.89	0.08	15.9	0.2	200	60	58.5	1.5	6.9	0.2	111	2
5/1-4	2.74	14.45	0.08	14.4	0.2	190	50	54.6	1.5	6.6	0.2	98	2
5/1-5	3.35	17.4	0.09	13.5	0.2	190	60	46.6	1.4	6.3	0.2	99	2
5/1-6	3.96	25.12	0.13	16	0.2	N.D.		44	1.5	5.9	0.2	109	2
5/1-7	4.27	22.71	0.11	17	0.3	N.D.		45	1.5	6	0.2	114	3
5/1-8	4.57	24.93	0.12	16.7	0.3	210	60	37	1.4	6.4	0.2	102	2
5/1-9	5.03	31.63	0.13	18.6	0.2	N.D.		40.5	1.4	4.4	0.2	118	2
5/1-10	5.49	42.16	0.15	26.3	0.2	N.D.		17	1.2	3.9	0.1	142	2
5/1-11	6.1	41.77	0.18	30.6	0.3	N.D.		16.9	1.4	4.9	0.2	159	3
5/1-12	6.71	41.11	0.17	32.4	0.3	N.D.		15.4	1.4	5.2	0.2	165	3
5/1-13	6.86	33.49	0.14	11.3	0.3	N.D.		N.D.		13.6	0.3	99	3
5/1-14	7.32	30.53	0.13	5.2	0.2	N.D.		N.D.		15.2	0.3	81	3
5/1-15	7.92	34.85	0.15	3	0.3	N.D.		N.D.		21.7	0.4	83	3

N.D. = not detected

TABLE XIV.

ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE

SEC 19, T. 5 N., R 1 W.

(continued)

SAMPLE NUMBER	DEPTH Meters	Cs	Error	Eu	Error	Ga	Error	Hf	Error	K	Error	La	Error
5/1-3	2.13	5.6	0.2	0.52	0.03	56	4	14.1	0.5	1890	60	21.2	0.3
5/1-4	2.74	5.5	0.2	0.51	0.03	64	4	15	0.5	1850	60	20.7	0.3
5/1-5	3.35	5.6	0.2	0.54	0.03	67	5	16	0.6	2000	70	20.2	0.3
5/1-6	3.96	4.5	0.2	0.59	0.04	83	6	19.1	0.7	1590	60	17.5	0.3
5/1-7	4.27	3	0.2	0.55	0.04	82	5	18.4	0.6	1420	60	17.1	0.2
5/1-8	4.57	2.1	0.2	0.48	0.02	89	6	18.8	0.6	1010	50	15.2	0.2
5/1-9	5.03	1.4	0.2	N.D.		106	7	22.9	0.8	560	40	10.6	0.17
5/1-10	5.49	0.4	0.1	0.18	0.02	132	8	26.6	0.9	100	30	5.16	0.1
5/1-11	6.1	0.5	0.2	0.36	0.04	114	7	28.6	1	100	30	4.87	0.11
5/1-12	6.71	N.D.		0.36	0.04	103	7	29.1	1	N.D.		4.74	0.11
5/1-13	6.86	N.D.		0.26	0.04	61	5	12.4	0.5	70	30	2.38	0.08
5/1-14	7.32	N.D.		0.3	0.06	59	5	11.3	0.5	N.D.		2.56	0.09
5/1-15	7.92	N.D.		0.32	0.07	55	5	11.5	0.5	110	40	3.82	0.1

N.D. = not detected

TABLE XIV.

ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE
SEC 19, T. 5 N., R 1 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Lu ppm	Error	Na	Error	Nd	Error	Rb	Error	Sb	Error	Sc	Error
5/1-3	2.13	0.21	0.02	293	2	13	3	35	6	1.5	0.1	17.65	0.08
5/1-4	2.74	0.24	0.02	264	2	11	3	39	7	1.48	0.1	21.62	0.08
5/1-5	3.35	0.23	0.02	270	2	11	3	N.D.	8	1.22	0.1	27.61	0.1
5/1-6	3.96	0.24	0.02	217	2	N.D.		42		1.57	0.1	31.74	0.11
5/1-7	4.27	0.2	0.02	222	2	N.D.		N.D.		1.42	0.1	25.3	0.09
5/1-8	4.57	0.19	0.02	171.2	1.8	9	3	N.D.		1.58	0.1	21.3	0.08
5/1-9	5.03	0.2	0.03	113.6	1.4	N.D.		N.D.		1.82	0.1	22.98	0.08
5/1-10	5.49	0.2	0.02	42.3	0.8	N.D.		N.D.		2.16	0.09	25.58	0.09
5/1-11	6.1	0.17	0.03	42.1	0.9	N.D.		N.D.		1.86	0.11	32.35	0.12
5/1-12	6.71	0.13	0.03	40.8	1	N.D.		N.D.		1.72	0.1	35.45	0.1
5/1-13	6.86	0.1	0.03	44.5	1	N.D.		N.D.		0.59	0.1	58.78	0.17
5/1-14	7.32	0.14	0.04	34.3	0.9	N.D.		N.D.		0.42	0.1	64.4	0.18
5/1-15	7.92	N.D.		48.2	1.1	N.D.		N.D.		0.36	0.11	86.3	0.2

N.D. = not detected

TABLE XIV.
ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE
SEC 19, T. 5 N., R 1 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Sm	Error	Ta	Error	Th	Error	U	Error	W*	Error	Yb	Error
5/1-3	2.13	3.34	0.03	2.7	0.2	20.4	0.2	6.2	0.5	1	0.15	1.6	0.2
5/1-4	2.74	3.47	0.03	2.4	0.2	21.3	0.3	7.5	0.5	1.12	0.14	1.4	0.2
5/1-5	3.35	3.6	0.03	2.8	0.3	20.4	0.2	7.1	0.5	1.1	0.16	1.5	0.2
5/1-6	3.96	3.28	0.03	3	0.3	24.1	0.3	6.9	0.5	1.13	0.15	1.3	0.3
5/1-7	4.27	3.27	0.03	2.8	0.3	21.4	0.3	6.9	0.5	1.02	0.14	1.4	0.3
5/1-8	4.57	3.03	0.03	3.1	0.3	22	0.3	8.3	0.5	1.13	0.16	1.2	0.3
5/1-9	5.03	2.34	0.03	4.2	0.4	25.4	0.3	6.9	0.5	1.38	0.16	N.D.	
5/1-10	5.49	1.33	0.02	5.1	0.4	28.4	0.3	6.1	0.4	1.61	0.18	N.D.	
5/1-11	6.1	1.26	0.02	3.9	0.4	34.2	0.3	6.1	0.5	1.26	0.16	N.D.	
5/1-12	6.71	1.24	0.02	3.7	0.3	35.4	0.4	5.9	0.5	1.11	0.15	N.D.	
5/1-13	6.86	1.29	0.02	1.9	0.2	13.1	0.2	5.5	0.4	0.4	0.11	N.D.	
5/1-14	7.32	1.02	0.02	1.6	0.2	9.5	0.2	5.4	0.4	N.D.		1.2	0.5
5/1-15	7.92	1.02	0.02	1.9	0.3	10.3	0.3	3.3	0.4	N.D.		N.D.	

N.D. = not detected

* W is normalized to sample 5/1-3

TABLE XIV.

ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE
SEC 19, T. 5 N., R 1 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Fe2O3 W%	Error	As ppm	Error	Ba	Error	Ce	Error	Co	Error	Cr	Error
Matrix separate													
5/1-3A	2.13	12.71	0.07	14.7	0.2	260	50	67.8	1.6	7.4	0.2	96	2
5/1-4A	2.74	11.58	0.07	12.7	0.2	210	50	58	1.5	6.5	0.2	86	2
5/1-5A	3.35	13.52	0.08	13.3	0.2	150	60	38.9	1.3	5.8	0.2	83	2
5/1-6A	3.96	12.96	0.08	12.8	0.2	200	60	42.4	1.4	5.9	0.2	80	2
5/1-7A	4.27	13.37	0.08	13.2	0.2	150	60	57.3	1.5	7.5	0.2	87	2
5/1-8A	4.57	12.42	0.07	11.8	0.2	N.D.		47.7	1.4	7.4	0.2	77	2
5/1-9A	5.03	10.41	0.06	11.3	0.2	N.D.		64	1.6	5.1	0.2	69	2
5/1-10A	5.49	20.56	0.1	16.4	0.3	N.D.		34.7	1.3	4.8	0.2	103	2
5/1-11A	6.1	25.18	0.13	22.7	0.3	N.D.		28	1.4	4.4	0.2	116	3
5/1-12A	6.71	25.32	0.13	19.4	0.3	N.D.		30.4	1.5	5.8	0.2	118	3
Iron pisolite separates													
5/1-3B	2.13	71.9	0.3	24.2	0.3	N.D.		14.3	1.4	4.7	0.2	593	6
5/1-4B	2.74	73.9	0.3	26.6	0.3	N.D.		17.5	1.5	3.9	0.2	283	4
5/1-5B	3.35	77.2	0.3	19.3	0.2	N.D.		N.D.		3.3	0.1	234	3
5/1-6B	3.96	72	0.3	24.2	0.3	N.D.		14.5	1.5	3.6	0.1	268	4
5/1-7B	4.27	72.4	0.3	29.1	0.2	N.D.		18.4	1.4	2.5	0.2	187	3
5/1-8B	4.57	73.1	0.3	27.3	0.3	N.D.		24.8	1.5	2.9	0.2	198	3
5/1-9B	5.03	65.5	0.2	30.7	0.3	N.D.		18.5	1.4	2.9	0.2	207	3
5/1-10B	5.49	62.9	0.2	34.5	0.3	N.D.		N.D.		3.4	0.2	186	3
5/1-11B	6.1	49.88	0.18	36.1	0.3	N.D.		N.D.		4.8	0.2	176	3
5/1-12B	6.71	63.7	0.2	30.6	0.3	N.D.		N.D.		4.2	0.2	205	4

N.D. = not detected

TABLE XIV.

ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE
SEC 19, T. 5 N., R 1 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Cs	Error	Eu	Error	Ga	Error	Hf	Error	K	Error	La	Error
Matrix separate													
5/1-3A	2.13	5.7	0.2	0.5	0.03	52	4	13.9	0.5	1860	60	20.6	0.3
5/1-4A	2.74	5.7	0.2	0.53	0.02	53	4	14.5	0.5	1800	60	20.6	0.3
5/1-5A	3.35	4.9	0.2	0.49	0.02	52	4	13.4	0.5	1800	70	18.8	0.3
5/1-6A	3.96	4.8	0.2	0.54	0.03	58	4	14.3	0.5	1830	70	19.4	0.3
5/1-7A	4.27	3.4	0.2	0.6	0.03	56	5	17.5	0.6	1770	70	21.8	0.3
5/1-8A	4.57	2.8	0.2	N.D.		63	4	17	0.6	1250	60	19.1	0.3
5/1-9A	5.03	1.6	0.2	0.49	0.03	74	5	18.1	0.6	800	50	12.5	0.2
5/1-10A	5.49	N.D.		0.2	0.02	108	7	27.7	0.9	210	50	6.61	0.13
5/1-11A	6.1	0.51	0.2	N.D.		97	6	28.1	1	160	30	5.22	0.12
5/1-12A	6.71	0.68	0.2	N.D.		76	5	23.8	0.8	280	40	5.06	0.12
Iron pisolite separates													
5/1-3B	2.13	2.1	0.2	0.44	0.04	206	12	30.3	1	320	40	6.63	0.13
5/1-4B	2.74	4.6	0.4	0.47	0.04	190	11	36.9	1.2	100	30	3.81	0.1
5/1-5B	3.35	0.7	0.2	0.35	0.03	172	10	27.5	0.9	N.D.		3.9	0.09
5/1-6B	3.96	0.9	0.2	0.47	0.04	164	10	32.8	1.1	170	30	4.6	0.11
5/1-7B	4.27	0.6	0.2	0.38	0.02	199	12	28.2	0.9	N.D.		4.23	0.1
5/1-8B	4.57	0.7	0.2	0.4	0.03	220	13	30.2	1	N.D.		5.01	0.11
5/1-9B	5.03	0.9	0.2	N.D.		158	9	30.1	1	110	30	5.16	0.11
5/1-10B	5.49	0.6	0.2	0.38	0.03	183	11	28.4	0.9	N.D.		4.38	0.11
5/1-11B	6.1	0.4	0.2	0.34	0.03	112	7	27.2	0.9	N.D.		3.85	0.09
5/1-12B	6.71	0.4	0.2	0.37	0.04	143	9	27.4	0.9	N.D.		3.46	0.09

N.D. = not detected

TABLE XIV.

ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE
SEC 19, T. 5 N., R 1 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Lu ppm	Error	Na	Error	Nd	Error	Rb	Error	Sb	Error	Sc	Error
Matrix separate													
5/1-3A	2.13	0.23	0.02	286	2	13	3	40	8	1.31	0.1	17.45	0.08
5/1-4A	2.74	0.23	0.02	263	2	14	3	36	8	1.25	0.1	21.31	0.08
5/1-5A	3.35	0.2	0.02	250	2	8	3	30	9	1.18	0.09	27.69	0.1
5/1-6A	3.96	0.23	0.02	246	2	14	3	24	7	1.13	0.1	28.54	0.1
5/1-7A	4.27	0.26	0.02	263	3	15	3	N.D.	0	1.31	0.1	21.04	0.08
5/1-8A	4.57	0.22	0.02	229	2	8	3	28	9	1.12	0.09	21.11	0.08
5/1-9A	5.03	0.18	0.02	150.3	1.8	N.D.		N.D.		1.11	0.09	20.53	0.07
5/1-10A	5.49	0.2	0.02	73.2	1.2	N.D.		N.D.		1.53	0.1	23.42	0.08
5/1-11A	6.1	0.14	0.03	58.2	1.2	N.D.		N.D.		1.45	0.1	28.92	0.1
5/1-12A	6.71	0.14	0.03	62.4	1.2	N.D.		N.D.		1.21	0.1	36.41	0.13
Iron pisolite separates													
5/1-3B	2.13	0.19	0.03	53.9	0.9	N.D.		N.D.		2.95	0.12	23.06	0.08
5/1-4B	2.74	0.17	0.03	35.8	0.7	N.D.		N.D.		2.25	0.11	32.2	0.12
5/1-5B	3.35	0.17	0.02	25.1	0.6	N.D.		N.D.		2.4	0.1	24.8	0.09
5/1-6B	3.96	0.19	0.03	39.9	0.8	N.D.		N.D.		2.46	0.11	29.98	0.11
5/1-7B	4.27	0.18	0.03	29.3	0.7	N.D.		N.D.		2.68	0.1	24.14	0.09
5/1-8B	4.57	0.19	0.03	32.1	0.7	N.D.		33	12	2.51	0.11	22.97	0.08
5/1-9B	5.03	0.17	0.03	37.4	0.8	N.D.		N.D.		2.82	0.11	25.06	0.09
5/1-10B	5.49	0.19	0.03	30.2	0.8	N.D.		N.D.		2.52	0.12	27.68	0.1
5/1-11B	6.1	0.12	0.03	38.3	0.7	N.D.		N.D.		1.99	0.09	34.72	0.1
5/1-12B	6.71	0.16	0.03	29	0.7	N.D.		66	16	2.27	0.11	33.73	0.12

N.D. = not detected

TABLE XIV.

ELEMENTAL CONCENTRATIONS IN THE COLUMBIA COUNTY CORE
SEC 19, T. 5 N., R 1 W.
(continued)

SAMPLE NUMBER	DEPTH Meters	Sm	Error	Ta	Error	Th	Error	U	Error	W*	Error	Yb	Error
Matrix separate													
5/1-3A	2.13	3.29	0.03	2.7	0.2	20.1	0.2	6.5	0.5	1	0.09	1.4	0.2
5/1-4A	2.74	3.52	0.03	2.5	0.2	20.5	0.2	7.1	0.5	0.99	0.09	1.4	0.2
5/1-5A	3.35	3.34	0.03	2.4	0.2	17.6	0.2	6.3	0.5	0.84	0.09	1.2	0.2
5/1-6A	3.96	3.58	0.04	2.5	0.2	18.1	0.2	6.6	0.5	0.84	0.09	1.6	0.3
5/1-7A	4.27	3.98	0.04	2.9	0.3	18.8	0.2	6.9	0.5	0.88	0.09	2.1	0.3
5/1-8A	4.57	3.61	0.03	3	0.3	18.2	0.2	9.1	0.6	0.85	0.09	1.3	0.3
5/1-9A	5.03	2.65	0.03	3.8	0.3	19.8	0.2	8	0.5	1.19	0.1	N.D.	
5/1-10A	5.49	1.77	0.02	6.6	0.5	26.8	0.3	8.1	0.5	1.77	0.14	1.4	0.4
5/1-11A	6.1	1.37	0.02	5.1	0.4	33.3	0.3	6.7	0.5	1.18	0.11	N.D.	
5/1-12A	6.71	1.33	0.02	3.3	0.3	31.2	0.3	5.9	0.5	0.78	0.09	N.D.	
Iron pisolite separates													
5/1-3B	2.13	1.62	0.02	4.1	0.4	41.6	0.4	5.6	0.5	1	0.09	N.D.	
5/1-4B	2.74	1.41	0.02	3.2	0.3	48.3	0.4	7.6	0.5	0.74	0.08	N.D.	
5/1-5B	3.35	1.19	0.02	3.6	0.3	34.8	0.3	4.3	0.4	0.96	0.1	N.D.	
5/1-6B	3.96	1.49	0.03	3.4	0.4	44.3	0.4	6.1	0.5	0.98	0.12	N.D.	
5/1-7B	4.27	1.21	0.02	4.3	0.4	34.8	0.3	4.7	0.4	1.01	0.09	N.D.	
5/1-8B	4.57	1.41	0.02	5	0.4	37.2	0.4	5.4	0.3	1.22	0.1	N.D.	
5/1-9B	5.03	1.41	0.02	4.7	0.4	36.4	0.4	5.8	0.5	1.09	0.1	N.D.	
5/1-10B	5.49	1.28	0.02	5.1	0.4	31.2	0.3	4.9	0.4	1.31	0.13	N.D.	
5/1-11B	6.1	1.1	0.02	2.8	0.3	34	0.3	4.8	0.4	0.63	0.07	N.D.	
5/1-12B	6.71	1.07	0.02	3.8	0.4	37.1	0.4	4.9	0.4	0.98	0.09	N.D.	

N.D. = not detected

* W is normalized to sample 5/1-3

APPENDIX D

TABLE XV

REPLICATION OF STANDARDS USED IN INAA

TABLE XV

REPLICATION OF STANDARDS USED IN INAA

	Pub- lished*				Pub- lished**			
	BHVO-1 Error	BHVO-1 Error	BQM1 Error	Value	Value	CRB1 Error	CRB1 Error	
	N.D.	N.D.	1.5	N.D.	N.D.	N.D.	N.D.	
As	(39.7)	(39.7)		73.7	1.5	68.8	52.6	1.1 52 1.2
Ce	47.4	0.2 47.6	0.5	45	11.7	0.1 11.7	37.2	0.4 36.9 0.2
Co	295	3 292	3	300	17.9	0.8 20.7	11.7	0.9 11 1.2
Cr	N.D.			0.086	5.93		6.6	1 0.13 0.81 0.15
Cs	(2.11)	(2.11)		1.03	0.02	1.19	1.92	0.03 1.86 0.03
Eu	(12.19)	(12.19)		4.65	0.03	5.13	12.83	0.05 12.54 0.05
Fe2O3	N.D.	N.D.	22	N.D.			N.D.	N.D.
Ga	(4.4)	(4.4)		4.91	0.18	5.4	4.46	0.17 4.33 0.19
Hf	N.D.	N.D.		0.55	4.4	0.5	4.3	1.44 0.24 2 0.3
K2O	17.1	0.3 16.5	0.3	16.7	(41)		28.3	0.4 25.6 0.4
La	(.25)	(.25)		0.24	0.02	0.31	0.4	0.02 0.4 0.03
Lu	2.25	0.02 2.25	0.01	2.21	2.91	0.02	3.28	3.11 0.01 3.28 0.02
Na2O	(24)	(24)		26	4	26	20.8	1.9 75 11
Nd	N.D.	N.D.		10		148	51	4
Rb	N.D.	N.D.		0.17	N.D.		N.D.	N.D.
Sb	(31.4)	(31.4)		10.51	0.04	11.43	30.98	0.07 30.21 0.09
Sc	(6.08)	(6.08)		5.25	0.05	5.79	6.59	0.04 6.09 0.04
Sm	(1.1)	(1.1)		0.67	0.08	1.01	0.66	0.11 0.64 0.11
Ta	1.24	0.11 1.28	0.1	1.1	20.49	0.18	18.7	5.58 0.1 5.39 0.12
Th	N.D.	N.D.		0.42	5.4	0.6	6.1	1.5 0.4 1.9 0.7
U	(2)	(2)		2	0.2	2.1	4.1	0 3.1 0.3
Yb								

Value in parenthesis is published value used in calculation of elemental concentration.

Standards were in two separate irradiations.

*BHVO published value determined by Gladney and Goode (1981).

**BQM 'published value' in Appendix E, Table XVI.

N.D. = not detected, N.A. = not analysed.

TABLE XV

 REPLICATION OF STANDARDS USED IN INAA
 (continued)

SRM- 1633A	SRM- Error	SRM- 1633A	Error	Pub- lished*	MAG1	Error	Pub- lished
1633A	Error	1633A	Error	Value	Value	Value	Value
As (145)		(145)		10	1.15	6	
Ce 185	3	179	4	180	80	0.8	94
Co (46)		(46)		19.8	1	20	
Cr (196)		(196)		129	14	105	
Cs (11)		(11)		4.3	0.3	8.3	
Eu 3.74	0.07	3.72	0.05	4	1.5	0.09	1.6
Fe203 13.11	0.06	13.14	0.09	13.44	7.07	0.08	2.6-4.2
Ga 58	5	72	12	58	N.A.	21.4	
Hf 7.3	0.3	6.7	0.4	8	3.9	0.13	3.6
K2O (2.26)		(2.26)			N.A.	3.6	
La 74.4	0.7	91	0.9	79	44	0.6	46
Lu 0.92	0.05	0.89	0.07	1.1	0.37	0.06	0.4
Na2O 0.25	0.01	0.19	0.01	0.23	N.A.	3.73	
Nd 61	5	N.A.		76	N.A.	44	
Rb (131)		N.A.			N.A.	152	
Sb (6.8)		(6.8)		1.06	0.16	0.91	
Sc 39.11	0.11	39.31	0.14	40	20.2	0.41	17
Sm 14.22	0.08	17.74	0.1	16.8	8	0.04	7.8
Ta 2	0.2	1.7	0.2	1.9	N.D.	1	
Th (24.7)	0.2	(24.7)	0.3	11	0.1	12.8	
U (10.2)		(10.2)		3.9	0.4	2.85	
Yb 7.1	0.7	8.5	0.8	7.5	N.A.	3	

Value in parenthesis is published value used in calculation of elemental abundance.

Standards were in two separate irradiations.

*SRM1633A values for La, Nd, Sm, Yb, Lu, and Ta determined at Portland State University.

TABLE XV.

REPLICATION OF STANDARDS USED IN INAA
RABBIT RUNS*
(continued)

	PUBLISHED				PUBLISHED			
	GSP 1	ERROR	GSP 2	ERROR AVE	VALUE	BHVO	ERROR	VALUE
TiO2	0.85	0.1	0.59	0.13	0.72	0.66	3.26	0.27 2.77
V	63.6	6	67.6	9	65.6	52.9	291	10 314
Al2O3	15.16	0.17	15.2	0.39	15.18	15.25	12.36	0.15 13.8
Mn	311	6	338	7	325	307	1190	25 1286

*SRM1633A was used as the primary standard for the rabbit runs.

APPENDIX E

TABLE XVI

BQM (BUTTE QUARTZ MONZONITE) ROCK

STANDARD CALIBRATION

TABLE XVI

BQM (BUTTE QUARTZ MONZONITE) ROCK
STANDARD CALIBRATION

	Split 3-4				Split 3-6				Aver-				Std. Dev.	Reference Standard
	BQM-A	BQM-B	BQM-C	BQM-D	BQM-E	BQM-F	BQM-G	BQM-H	BQM-I	BQM-J	BQM-K	age		
Ba	760	870	830	900	850	780	870	860	880	750	790	831	50	GSP-1
Ce	61	67.5	72.9	67.7	75	76.8	74.8	72.3	72.6	56.3	59.8	68.8	6.6	GSP-1
Co	11.1	11.9	11.7	12.3	11.6	11.5	11.7	12.3	12	11.7	11.3	11.7	0.4	SRM1633A
Cr	19.7	23.2	23.4	21.2	22.6	18.4	21	22	19	17.1	20.3	20.7	1.9	SRM1633A
Cs	6.4	7.1	6.8	6.6	6.6	6	6.7	6.9	7.1	6	6.7	6.6	0.4	SRM1633A
Eu	1.17	1.19	1.22	1.24	1.17	1.17	1.16	1.28	1.23	1.1	1.2	1.19	0.05	GSP-1
Fe203	4.72	5.28	5.09	5.21	5.22	5.07	5.29	5.34	5.21	4.92	5.04	5.13	0.18	BHVO-1
Hf	4.9	5.1	5.1	5.5	5.7	5.6	4.8	6.3	5.7	5	5.6	5.4	0.4	GSP-1
K2O	4.5	3.8	3.8	4.3	4.4	4.6	4	4.1	4.8	4.5	4.6	4.3	0.3	GSP-1
La	43.3	36.2	42.8	40.9	42.7	45.9	37.4	43.1	41.5	37	40	41.0	2.9	GSP-1
Lu	0.28	0.3	0.29	0.33	0.33	0.27	0.34	0.33	0.33	0.28	0.29	0.31	0.02	BHVO-1
Na2O	3.39	2.87	3.35	3.44	3.4	3.31	3.11	3.41	3.31	3.16	3.33	3.28	0.16	GSP-1
Nd	26	26	29	23	31	26	26	28	27	24	20	26	3	GSP-1
Rb	136	145	147	155	160	151	144	152	160	139	139	148	8	GSP-1
Sc	10.75	11.76	11.32	11.76	11.5	11.24	11.5	11.89	11.62	11.09	11.3	11.43	0.32	BHVO-1
Sm	5.99	4.86	5.82	6.02	5.96	5.9	5.7	6.1	6.2	5.32	5.8	5.79	0.37	GSP-1
Sr	400	510	620	480	460	310	550	410	330	330	300	427	101	SRM1633A
Ta	0.9	1.1	1	1.1	1.2	1.1	1.2	1.4	1.1	0	1.06	1.01	0.34	GSP-1
Th	14.9	21.5	17.7	18.2	26.2	18.7	15.7	21	19	17	16.2	18.7	3.1	GSP-1
Yb	2.1	2.2	1.9	2.4	2	2.1	1.8	2.1	2.4	1.9	1.8	2.1	0.2	BHVO-1