ALS METHODS
ME-VEG41™
ME-VEG41a™

Biogeochemistry

Plants take up trace elements from soil and bedrock at depth, providing an accessible surface sampling medium for the exploration of buried deposits.

Geochemical exploration in covered terrain requires the ability to measure and detect mineralisation at depth, and to separate the mineralisation signature from baseline geochemical variations in surficial rocks or soils. Plants have long been recognised as a medium that can produce a geochemical response from the substrate by concentrating elements within plant tissues, thereby providing a uniform sampling medium capable of indicating mineralisation.

There is a wide range of economic and pathfinder elements that are absorbed by plant systems, which can be effectively measured by the chemical analysis of various plant parts. Once species selection, geographical distribution, tissue type, and sample size have been considered in the context of an exploration program, sample collection is easy and may cover a large geographical area more quickly than a soil survey. Because of the wide lateral reach of many root systems, anomalous targets that could be missed in a widely-spaced soil grid have a better chance of biogeochemical detection and may be quickly followed up with more detailed soil sampling or trenching.

Ecological Environment

The ecological environment greatly affects the role that plants have in geochemical dispersion and concentration. Plant roots may sample groundwater, soil or rock through

the production of organic acids at the root tips, dissolving minerals and allowing the plant to uptake nutrient elements as well as waste elements that are subsequently segregated into various plant parts. Boreal and deciduous forests, grasslands and highlands, hot and cold arid regions, and all other climate zones will have different species that are more suitable for geochemical sampling than others and different key elements by which the plants reflect geochemical anomalies.

In arid terrain, plants must have enormous root systems in order to reach groundwater sources. As a result, these plants sample large volumes of soil, rock and groundwater and are particularly effective for identifying geochemical anomalies in the surficial environment. In the Basin and Range province of Nevada, USA, sagebrush provides a uniform sampling medium across vast areas. Numerous vegetation sampling programs conducted or supported by Smith (2005) document significant biogeochemical responses around gold deposits in Nevada.

In glaciated terrain, bark and twigs of trees such as fir, pine, spruce and birch have proven to be excellent accumulators of pathfinders to many deposit types. Plants in this environment act as an effective complexing agent, capturing and concentrating metals in a similar fashion to oxide species in a well-developed B-horizon soil. Dunn (2007) documented numerous examples of rapid helicopter-based tree top collection of spruce throughout forested regions of Canada which produced anomalous geochemical targets for further investigation.

Sampling Vegetation

The geographic coverage of the plant species of choice should be adequately uniform so that plants may be sampled on a soil survey style grid. Because different species do not uptake elements in the same way, species cannot be mixed within a survey. The concentration of elements varies between different plant parts and seasons within a species. An understanding of how different plant species metabolize potential elements of interest to exploration geochemistry (for example, Zn) should be taken into account when selecting the target species.

Sampling vegetation is generally simple and fast. Consistency in stage of growth and individual plant health while sampling is key to a successful survey. As with water sampling, trace contamination is extremely important. The same duplicate protocol that is commonly used in soil sampling may be applied to vegetation sampling, and one or more appropriate reference samples submitted for quality control. The sample weight required for analysis varies by analytical method, but a general rule of thumb is a minimum of 200g wet sample weight. Samples should be collected in cloth bags, not plastic, to promote drying and prevent rot before reaching the laboratory.

For an in depth discussion of specific species in global exploration regions and detailed sampling guidelines, please consult **Biogeochemistry in Mineral Exploration (Handbook of Exploration and Environmental Geochemistry, Vol. 9: Colin E. Dunn, 2007).**

Sample Preparation and Analysis

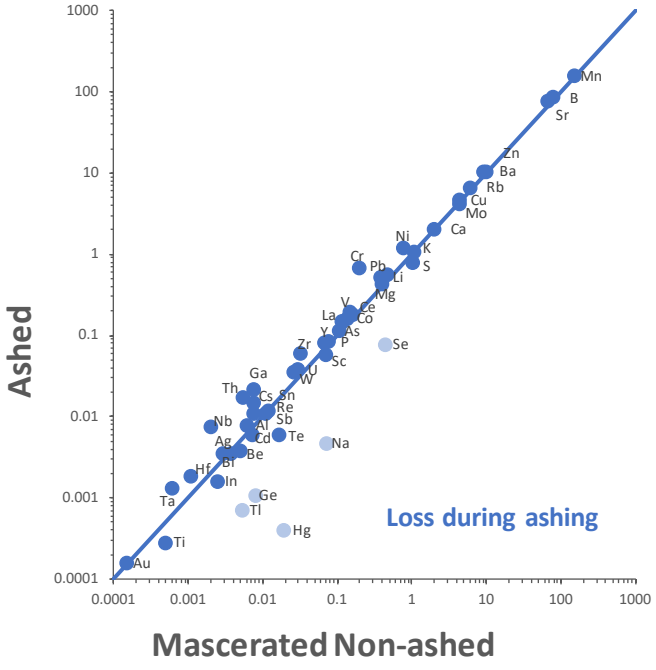
Preparation of samples may include sorting of different tissue types, drying, and maceration in specialised milling equipment. Gentle washing to remove dust and pollen is also offered although it is not usually required and if needed should be used with caution due to the potentional to remove surface tissues that can contain important element concentrations. Exact sample prep specifications will vary according to the plant species, type of tissue collected, and the analytical method of choice.

METHOD	ALS CODE	DESCRIPTION
Sample Preparation	VEG-MILL01	Milling of dry plant tussue to 100% passing 1mm. Produces a homogenous sample for representative subsampling and analyses.
Sample Preparation	VEG-ASH01	Vegetation sample is ashed at 475°C for 24 hours. Pre- and post-ashing weights are reported. Average ash yields are 2-4% for species commonly used in exploration surveys. Minimum recommended sample weight is 100g.
HNO_3/HCl Digestion	ME-VEG41™	Nitric/hydrochloric acid digestion and ICP-MS measurement, 65 elements, using 1g of finely milled material.
HNO_3/HCl Digestion	ME-VEG41a™	Nitric/hydrochloric acid digestion and ICP-MS measurement, 65 elements, using 0.25g of ash material.
HNO_3/HClDigestion	VEG41a-FAC™	Results from a ME-VEG41a™ analysis back calculated to original concentration using pre-ash weight.
Aqua Regia Digestion	VEG41-REE™	Nitric and HCl digestion of 1g of macerated plant matter with ICP-MS analyses for super trace REE. Add on only.
Aqua Regia Digestion	VEG41a-REE™	Aqua regia digestion of 0.25g of ash sample with ICP-MS analyses to produce super trace REE. Add on only.
Halogens (F-Br-Cl-I)	ME-HAL01a™	Semi-quantitative analysis for the halogens in plant tissues. A distilled water leach on 0.25g of ash sample is analyzed by a combination of Ion Chromatography and ICP-MS.

To Ash or Not to Ash

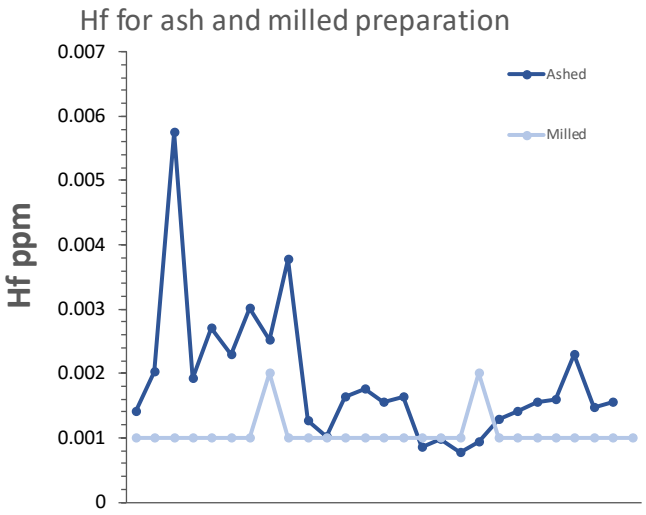
When using biogeochemistry for exploration one of the main decisions when planning a program is whether to ash samples before analysis or not. Ashing is the process by which biogeochemical samples are heated at 475°C for 24 hours to reduce their weight and preconcentrate elements of interest (ALS code VEG-ASH01). The alternative preparation method is to mill a dry biogeochemical sample so that it can be sub-sampled for analysis (ALS code VEG-MIL01). Each has their advantages; non-ashed samples represent the concentrations of all elements, even those that are volatile during heating; whereas ashed samples pre-concentrate most elements resulting in fewer or no samples with values below detection. By ashing biogeochemical samples before analysis, the detection level for most elements is effectively lowered. ALS reports results as both a raw analysis result and a calculated concentration based on the pre- and post-ash weights (VEG41a-FAC™).

Mercury is the only element that is completely lost during the ashing process; the very few elements that are partially volatilised, and the extent to which those elements are lost, is due to factors such as the vegetation type and the chemical compound in which an element is present. Any losses tend to be consistent because we have a controlled ignition phase for the ashing process. There are numerous studies of biogeochemical sampling that have investigated how elements are retained and lost during ashing for different species. A list of biogeochemistry references can be obtained from ALS on request to assist in refining your search. Where a study is available for a plant species there should be no need for additional pre-testing at your exploration project; however, when using a species for which there is no documented investigation, it would be prudent to do a comparative study of ashed versus milled sample concentrations.



The mean of 27 samples for both ashed and milled preparation showing the changes in element concentration.

An example of where the two sample preparation options have been applied to a selection of Australian vegetation is described here, although these element relationships will not be the same for all species. From this sample group the elements that showed a reduction in the number of results reported below detection after ashing are listed in the next table, and significantly include Au and other elements of interest to explorers. From the same sub-set, elements Hg, Tl and Ge show substantial depletion after ashing with more results reporting below detection. The decrease in concentration of these elements is due to their volatility during the ashing process.



For most elements the concentration is a near linear trend between the pre-ashed sample and the post-ashed sample with more significant figures for data reported on ashed analyses. As concentrations are generally low in biological materials, the ability to push the detection limits lower increases the number of samples above background, and the confidence in anomalies. It also increases the number of elements that produce meaningful data and can therefore be used in targeting.

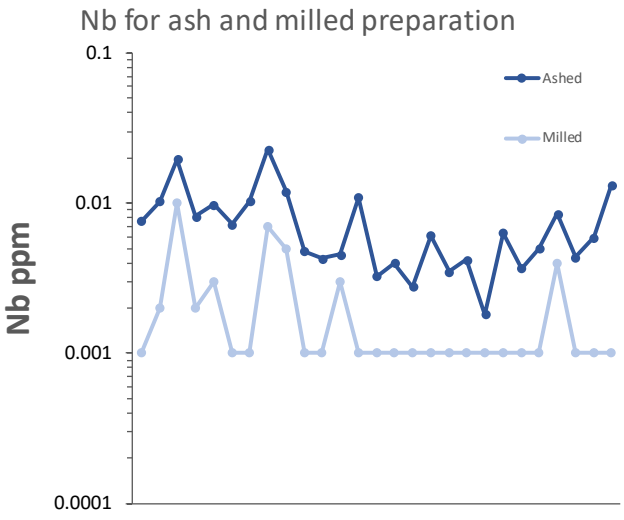


Table 1: List of elements for which there is a change in the number of samples reporting below detection for a data set that has both ashed and unashed analyses on Australian vegetation.

Element	Ashed below detection	Non-ashed below detection	Change
Be	0	27	27
Ti	0	27	27
Hf	0	25	25
Al	0	21	21
Au	0	19	19
Nb	0	19	19
Sn	0	17	17
Cs	0	16	16
U	0	16	16
Ta	9	23	14
In	13	27	14
Th	0	10	10
Ga	0	8	8
Li	0	4	4
Cd	6	10	4
Te	13	17	4
Sb	0	3	3
Pt	25	27	2
Bi	0	1	1
W	0	1	1
Zr	0	1	1
Ge	5	1	-4
Tl	10	4	-6
Hg	20	0	-20

Halogens

Numerous lines of evidence suggest that halogens play an important role in ore deposit formation and thus will be indicative of the presence of ore systems where they are found in anomalously high concentrations. The evidence for the role of halogens in ore systems is threefold. Firstly, halogens are found in fluid inclusions from ore deposits which are preserved bubbles of the mineralising fluids and show that halogens were part of these fluids. Secondly, Cl and F present in the crystal structure of minerals associated with mineralisation. An example from the Kristineberg volcanogenic massive sulfide district, Sweden, is of high fluorine in muscovite and phlogopite associated with mineralisation (Hannington et al., 2003). Thirdly, halides are thought to be responsible for complexing metals and transporting them in hydrothermal solutions during the formation of ore deposits.

The pre-ashing of biogeochemical samples is essential for halogen analyses due to the very low concentration of these elements in plants, and to remove interferences caused by organic compounds. Even with the volatilisation of the halogens during ashing, the ashed samples generally report concentrations within the detection limits. Analyses of halogens is not quantitative so is applicable only as an exploration tool where the comparison of relative concentrations is useful.

ME-VEG41™ ANALYTES & DETECTION LIMITS (ppm)							
Ag	0.001	Cu	0.01	Nb	0.002	Ta	0.001
Al	0.01%	Fe	1	Ni	0.04	Te	0.02
As	0.01	Ga	0.004	P	0.001%	Th	0.002
Au	0.0002	Ge	0.005	Pb	0.01	Ti	0.001%
B	1	Hf	0.002	Pd	0.001	Tl	0.002
Ba	0.1	Hg	0.001	Pt	0.001	U	0.005
Be	0.01	In	0.005	Rb	0.01	V	0.05
Bi	0.001	K	0.01%	Re	0.001	W	0.01
Ca	0.01%	La	0.002	S	0.01%	Y	0.003
Cd	0.001	Li	0.1	Sb	0.01	Zn	0.1
Ce	0.003	Mg	0.001%	Sc	0.01	Zr	0.02
Co	0.002	Mn	0.1	Se	0.005		
Cr	0.01	Mo	0.01	Sn	0.01		

References and Further Reading

Dunn, C.E. 2007. Biogeochemistry in Mineral Exploration. Handbook of Exploration and Environmental Geochemistry 9. Series Ed. M. Hale. Elsevier, Amsterdam, The Netherlands, 462 pp + CD.

Hannington, M.D., Kjarsgaard, I.M., Galley, A.G., and Taylor, B., 2003. Mineral-chemical studies of metamorphosed hydrothermal alteration in the Kristineberg volcanogenic massive sulfide district, Sweden. Mineralium Deposita, issue 38, pp423-442.

Smith, S.C., and Vance, R.B., 2005. Discovery using metal concentrations in plants, Rosebud Mine, Pershing County, Nevada, in Rhoden, H.N., Steininger, R.C., and Vikre, P.G., eds., Geological Society of Nevada Symposium 2005; Window to the World, Reno, Nevada, May 2005, p. 1225-1240.

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GEOCHEMISTRY CLIENT SERVICES

Australia/Asia — Brisbane
T +61 7 3243 7222
E alsgeo.brisbane@alsglobal.com

Australia/Asia — Perth
T +61 8 9347 3222
E alsgeo.perth@alsglobal.com

Africa — Johannesburg
T +27 11 608 0555
E alsgeo.johannesburg@alsglobal.com

Brazil — Belo Horizonte
T +55 31 3045 8400
E alsgeo.belohorizonte@alsglobal.com

Canada — Vancouver
T +1 604 984 0221
E alsgeo.vancouver@alsglobal.com

Chile — Santiago
T +56 2 2654 6100
E alsgeo.santiago@alsglobal.com

Europe — Loughrea
T +353 91 841 741
E alsgeo.loughrea@alsglobal.com

Europe — Seville
T +34 955 513 035
E alsgeo.seville@alsglobal.com

Mexico — Hermosillo
T +52 662 260 7586
E alsgeo.hermosillo@alsglobal.com

Peru — Lima
T +51 1 574 57 00
E alsgeo.lima@alsglobal.com

Ecuador-Quito
T: +593 2 513 0891
E: alsgeo.quito@alsglobal.com

USA — Reno
T +1 775 356 5395
E alsgeo.reno@alsglobal.com