Theory behind the use of soil pH measurements as an inexpensive guide to buried mineralization, with examples

Introduction

The controversy about the use of selective or weak extractions (SWE) to detect buried or blind mineralization continues unabated. Proponents of the methods often appear to be associated with the companies that offer the analytical services (Birrell, 1996; Clark, 1993; Mann et al., 1998) whilst studies that reveal the difficulties in using such methods are primarily from arms-length institutions (Bajc, 1998; Gray et al., 1999; Seneshen et al., 1999; Smee, 1997). I expect the debate will continue into the foreseeable future.

The principal uncertainty with SWE is the lack of a solid understanding of the geochemical transport processes that might give rise to interpretable element patterns. This understanding is critical in order to produce predictable results from a particular mineralized target. Additionally, without this knowledge it is not possible to select the most appropriate SWE method for each climatic and geological environment, or choose the most revealing method of interpretation.

Background

Whatever the transport process, at least one ion of interest must move through cover in order to be used for mineral exploration. Ions might move in solution, by seismic pumping along fractures (a form of diffusion), by gaseous

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**Figure 6:** Copper contour overlain on calcium as 3D relief map, Oyu Tolgoi, Mongolia. The major copper anomalies caused by sulphide mineralization are surrounded by high calcium. Calcium is absent from the immediate area of the mineralization.

**Figure 1:** Location of the Kirkland Lake and Lake Timiskaming kimberlite fields in northeastern Ontario and the five kimberlites sampled in this study: 1) B30; 2) C14; 3) A4; 4) Diamond Lake; 5) 95-2. Bedrock geology from Ontario Geological Survey (1991).

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Groundwater Interaction... continued from Page 1

Geology

Of the five kimberlites sampled, four are within the Kirkland Lake kimberlite field (A4, B30, C14 and Diamond Lake) and the other (95-2) is in the Lake Timiskaming kimberlite field (Figure 1). The geology surrounding these kimberlites is very similar and all are of the same approximate age (155 to 160 Ma). The host rocks are Archean mafic to felsic volcanics and felsic to intermediate intrusives, intruded by Proterozoic mafic dykes (Jenson, 1975). At the time of kimberlite emplacement, the area was overlain by Paleozoic carbonates (Brunner et al., 1992b) as well as Proterozoic (Huronian) siltstone at kimberlite 95-2.

Field and Analytical methods

Groundwaters were collected from previously drilled exploration holes. Groundwater pH, conductivity, oxidation-reduction potential (ORP), dissolved oxygen and temperature were measured in the field. A number of sampling methods were used, including sliding-head straddle-packer, Grundfos electric pump and double-valve pump. Nitrogen gas was used to drive a column of water from depth to the surface for the double-valve pump and packer system. Groundwater was sampled from the overburden-kimberlite contact (40 to 60 m depth) down to approximately 200 m.

Geochemical Results

Groundwater pH values are higher than is typical for groundwater in crystalline rocks and the average for all samples is 9.54. Groundwater pH values are as high as 12.4 in the A4 kimberlite (Figures 2, 3). The highest pH values are consistent with low-temperature serpentinization reactions involving hydration of ultramafic minerals (Clark and Fritz, 1997) and the formation of hydroxide alkalinity, CH₄ (methane) and H₂ (Deines and Langmuir, 1974).

![Figure 2. Iron and sulfur stability fields and location of kimberlite water samples.](image-url)
Groundwater Interaction...

Possible reactions include (Sherwood Lollar et al., 1993) (Equations 1, 2):

\[ \text{Olive} + H_2O + C \text{ (or } CO_2) = \text{magnetite} + \text{serpentine} + CH_4 + \text{brucite} + H_2 \]  
\[ 5\text{MgSiO}_4 + 8\text{FeSiO}_4 + 8H_2O = 3\text{Mg}_2\text{Si}_2\text{O}_7(\text{OH})_2 + \text{Mg(OH)}_2 + 2\text{Fe(OH)}_3 \]

The Eh values for groundwater from the five kimberlites have an average of 80 mV. However, many of the waters are reducing coincident with high pH values (Figure 2). Groundwaters from the A4 kimberlite, which yielded the highest pH values and were the most gas-rich, yielded the lowest Eh values (as low as -536 mV).

To date, the groundwaters have been analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) for Ca, Mg, Na, K, Si, Al, As, Ba, Cu, Fe, Li, Mn, Mo, Se, Sr and Zn and by isotope ratio mass spectrometry for O, H and C isotopes. Groundwater samples are in the process of being analyzed by ICP-MS (mass spectrometry) for a full suite of trace elements, S isotopes on sulfate and sulfide, and Pb and Sr isotopes by thermal ionization mass spectrometry. The stable-isotope data and major elemental analyses strengthen the argument that these waters are unusual with respect to other natural waters.

The kimberlite-associated groundwaters are unusual in that the K/Mg ratio is large and directly proportional to pH (Figure 3), suggesting that Mg is being buffered, whereas K is not. In most groundwaters, K is typically controlled by clay formation (e.g. illite). Mg is likely locked in alteration minerals such as brucite [(Mg(OH))_2] and serpentine [MgSi_2O_5(OH)_4], which can be supersaturated in waters associated with ultramafic rocks (Barns and O'Neil 1969, Barns et al., 1972). Potassium contents in the kimberlite groundwaters reach 39,600 µg/L and Mg values are as low as < 0.1 µg/L. Kimberlite A4 is anomalous and has the most consistently high K (average 16,100 µg/L) and low Mg contents (average 27.4 µg/L).

The δ^4_HVSMOW and δ^18O_VSMOW range from -90 to -125‰ and -13.5 to -18‰ respectively (Figure 4). The heaviest values are consistent with modern recharge for this part of Canada (between -13 and -14‰ for δ^18O_VSMOW; Clark and Fritz, 1997). The isotopically lighter waters may represent paleowaters recharged under a different climatic regime. Additionally, groundwaters from the A4 kimberlite do not fall along the Ottawa meteoric water line (OMWL); calculated from data from the International Atomic Energy Agency [IAEA] Isotope Hydrology Section database: http://isohis.iaea.org (Figure 4). The deviation of the A4 groundwaters may reflect fractionation during H_2 and CH_4 production (Equation 1), however this is likely only a very minor component. Another explanation is that the
production of large amounts of OH in the waters is causing an enrichment of the δ18H. It is also likely that there has been mixing between modern recharge and older waters. The longer period that the waters have had to react with the rock would also help to explain why the waters have elevated pH, low Eh and high gas contents with respect to the other kimberlite waters, consistent with the strong correlation between δ18H and pH (Figure 5).

Figure 5. For all samples but A4, there is a correlation between pH and H (and O) isotopic composition.

Conclusions
Our initial data and interpretations are extremely encouraging with respect to developing hydrogeochemistry as a kimberlite exploration tool. Groundwaters associated with kimberlites are clearly unusual with respect to Eh-pH relationships, K and Mg contents and K/Mg ratios. These geochemical features alone permit discrimination between waters interacting with ultramafic rocks and those interacting with other lithologies. We anticipate that the pending trace element and radiogenic isotope data will help refine our interpretations of water-kimberlite interactions and will also assist in refining methods for utilizing groundwater geochemistry in kimberlite exploration. For more information please visit the GSC website.

References


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Past President's Message

Ladies and gentlemen,

May I start by wishing all members of AEG a Happy, Healthy and Prosperous New Year? The past year, during which you have honoured me by letting me serve as your president, has flown by and I now hand over the AEG presidency into the hands of Steve Amor. Steve has been a very active member of AEG; he played the key role of AEG Webmaster, managing our website that has become a very powerful tool for our Association. Steve is also the chairman of the Symposium Committee, coordinating all AEG actions for organizing the IGES conference. He intimately knows AEG’S heart and how it ticks, and I have no doubt that he will be a dynamic president for this coming busy year. Bonne Chance Steve, I wish you a successful 2003!

2002 has been a key year for AEG, which saw profound changes in our organization. Thanks to the efforts of Nigel Radford and David Garnett, there has been real progress in updating the Association By-Laws. Fellow members not only had to cast their usual vote for replacing AEG Council members, but they also voted on fundamental questions that will most likely strongly influence AEG’s evolution over the next years.

The debate on enlarging the scope of our Association to include environmental aspects has been successful and can be considered closed. In fact, over 90% of voters were in favour of this change and accepted that the new purpose of the Association now can be summarized as follows: “To advance the science of geochemistry especially as it relates to the geochemistry of mineral resources – their exploration, exploitation, and environmental impact”. This great majority clearly shows that our members wish to integrate the new problematics concerning the environment and to open the scientific debate to other aspects than those traditionally covered by mineral exploration. However, I think it indispensable that we retain our cultural and professional roots, which implies that the main thrust of environmental geochemistry should by and large be associated to the environmental impact of mining mineral resources.

Furthermore, and in view of this enlarged field of action for AEG, 81% of you consider that our Association would require a new name to become more visible and representative of its scientific field. I consider this to be a very positive and encouraging sign for the future. According to the Statutes, a two-thirds majority is needed for such changes. The AEG will thus change its name, which is a historical turning point that well illustrates how our profession as geochemists is evolving.

Finally, for the third proposal of a vote for the new name of our Association, two choices were retained: “Association of Applied Geochemists” and “Association of Exploration and Environmental Geochemists”. A clear majority of 62% voted for the second proposal. Not only would this new name AEG be the reverse of the title of our new journal (GEEA), but it also clearly shows the thematic field of environmental geochemistry. However, during the last General Meeting of November 20th, 2002, we were unable to change the name because our Statutes indicate that a two-thirds majority is required. We thus lacked a few votes this year, but a new voting procedure will be proposed to fellow members in early 2003 in order to validate the choice of the membership. I sincerely hope that we will be able to toast this new name during our next AGM at Dublin, next September.

As you may have read in the last issue of EXPLORE, Wendy Hall’s dynamism and enthusiasm for launching our new journal GEEA—the first issues of which were a success—could not avoid problems with our publisher, who was unable to distribute on time the four issues planned for 2002. Apparently, these problems now have been solved and I hope that when you read these lines the missing 2002 GEEA issues will be in your hands. GEEA is the scientific heart of our Association, and it is essential for our journal to become the reference for exploration geochemistry and environmental geochemistry. To attain this goal and to rapidly reach a financial equilibrium, we need your mobilization for proposing papers and suggesting to your libraries that they should subscribe to GEEA.

2002 was also a key year for our newsletter EXPLORE. Its size increased significantly and colour made its appearance. It has been decided at the last council meeting that, in order to heighten our association’s profile and attract new members, EXPLORE will be now be freely accessible to non-members on our website. This represents a major shift in the concept of our newsletter, marking our wish to open to all the issues that concern us as geochemists. These changes are particularly due to the introduction of corporate sponsorship, which has substantially increased the newsletter’s budget. Electronic versions can already be downloaded from our website, and full electronic circulation of EXPLORE is planned for very soon. I would like to thank Mary Doherty and the editorial board, who have done a great job in making EXPLORE ever more attractive and innovative.

Before handing over to Steve Amor, I would like to take this final opportunity to exhort you all to take an active part in the Association. It is your association: take part in the debates, write an article for EXPLORE, add a contact to the website, submit a manuscript to GEEA. Above all, try and get your colleagues to join AE(E)G and make it increasingly relevant to our dynamic and exciting scientific discipline. I strongly believe mineral exploration will face profound changes in the near future, thanks to technological advances that will lead to major new discoveries. As for environmental geochemistry, this is a fairly recent discipline with an extraordinary scope for progress.

Best wishes and good luck to all exploration and environmental geochemists, and thanks again for having me as your president.

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AEG Presidential Address

I would like to thank Philippe for his kind remarks and would like to be worthy of them. We all owe Philippe a debt of gratitude for his stewardship of our association during this critical period. The requirements of my new job, in a field completely unrelated to geochemistry, prevented me from attending the recent joint AGM/Council meeting. Therefore, other than the debate over our name change, and the quite reasonable concerns that many members have shown as to the effect this will have on our mission, I am not as aware as I should be as to most of the issues of current interest to geochemists.

As a Council member who has had time on his hands, and knowledge of the Internet, whose peers thereby judge him to be capable of leading an international organization, I consider myself to be the personification of a certain principle advocated by Dr. Lawrence Peter; nothing would have pleased me more than to be allowed to continue pottering along at something I was reasonably good at.

When I was approached by Nigel Radford in early 2001 as to whether I would accept the position of AEG’s Second Vice-President (thereby climbing onto the conveyor belt that has brought me to the Presidency in 2003) I raised the possibility, which seemed adequately remote (hence my agreement), that the AEG might be soon headed by a non-geochemist if there was a continuation in this period of reduced demand for our services. A worst-case scenario, perhaps, but what has transpired is not far from that. As 2002 draws to a close I and many explorationists have been unable to support themselves and their families, through their chosen profession, in half a decade. Even with the recent recovery in the gold price (taking it back, incidentally, to levels not seen since mid-1997; there are instructive charts at http://futures.tradingcharts.com/chart/GD/M and http://www.gold-eagle.com/charts/35yeargold.html) indications of sustained interest on the part of the mining industry in hiring more exploration professionals are hard to detect.

However, the last few issues of EXPLORE, and the upcoming one, have shown that not only is there a core of geochemists who have maintained a presence in the workforce, but that they are willing and able to pass on the benefits of their experience in lucid and instructive form. I look forward to overseeing the continued expansion of this role for the newsletter. Its public access on the website can only be good for the Association, and our discipline in general.

While still on the subject of the Website I would like to take advantage of this forum to make a pitch for a pet (albeit dormant) project of mine, the online queriable bibliography. In order to make this a reality (and what a boost for the Association that would be!), it is necessary to assign keywords to every one of the approximately 15,000 citations that the bibliography already contains, and all subsequent ones; doing an online search based on strings of text is simply too slow. This daunting task would become manageable if 150 AEG members agreed to read the abstracts of 100 papers, select appropriate keywords and communicate them to the Webmaster. I will be relinquishing this position, incidentally, and my replacement will have been appointed by the time you read this piece, although his or her name is unknown to me as I write it.

During my Presidency I would like to see the expansion of our Association’s terms of reference taken to its next logical step: a significant number of geochemists must join us, who consider themselves to be primarily environmental in orientation. Those current members, who come into regular contact with our environmental counterparts, should be doing what they can to persuade the latter of the benefits of membership. The need for the consolidation of GEEA’s role and sphere of influence hardly needs reiterating; and we must be unremitting in our attempts to persuade our employers and potential employers that effectively-applied geochemistry is not an expensive luxury, nor a black-box application to give the illusion of thorough scientific study to a gullible investor, but a rigorous and effective procedure, the investment in which makes sound economic sense.

I wish everyone a rigorous and effective 2003, and look forward in particular to working with my Vice-President Dave Kelley. And to wishing slainte to you all in Dublin in August.

Steve Amor
AEG President
2003
Election Results: The result of the recent AEG elections for new Council members (2003-2005) and the motion regarding the proposed change in the Preamble to the By Laws and a change in name for the Association (see EXPLORE No. 116), were announced at the 2002 Annual General Meeting. Approximately 47% of AEG Fellows voted in this election. The vote for the Change to the Preamble to the By Laws was:

In Favor of the change: 102, against the change: 9.

The results for the motion to Change the Name of the Association:

In favor of a name change: 91, opposed to a name change: 20.

The result of the question regarding the New Name of the Association: Association of Exploration and Environmental Geochemists: 56 votes, Association of Applied Geochemists: 34 votes. David Garnett, chair of the By Laws Committee, will draft a revised version of the By Laws including the approved change to the Preamble as well as other changes recommended by the By Laws Committee. These changes will be sent to Council for final revision and then submitted to AEG Fellows for a formal vote. On the same ballot, but as a separate item, "Association of Exploration and Environmental Geochemists" will be submitted for approval as the new name of the Association. For either of these issues to pass, it must receive approval by at least two-thirds of the voters. If the proposed new name is not approved, Council will reopen discussions on this issue. Council hopes to have the revised By Laws ready for publication in the April 2003 issue of EXPLORE. A formal ballot containing motions to approve these changes and the name change will be sent to Fellows shortly thereafter.

The new Council members elected for 2003-2005 are: Rob Bowell, Allan Kelly, Chris Oates, David Seneshen, Cliff Stanley.

AEG wishes to thank all the candidates who stood for election and all the outgoing Council members for their willingness to serve the Association.

David B. Smith, Secretary AEG

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HYDROTHERMAL ALTERATION ZONES AT TWO MASSIVE
SULPHIDE DEPOSITS: CONTRASTS IN
LITHOGEOCHEMICAL EXPRESSION DUE TO
HOST ROCK CONTROLS

The Grizzly Zn-Pb sediment-hosted massive sulphide
deposit, Faro Yukon, is hosted by lower Paleozoic,
fine-grained clastic rocks of the Selwyn basin. The Halfmile Lake
Cu-Zn-Pb volcanic-hosted massive sulphide deposit,
Bathurst, New Brunswick, is hosted by lower Paleozoic
volcanic and volcanioclastic rocks of the Teteagouche-Exploits
back-arc basin. Hydrothermal alteration and associated
metasomatism in the host rocks to these deposits have been
investigated with molar element ratio analysis using two
substantial lithogeochemical datasets collected from drill
core through these deposits. Results illustrate distinct
alteration and metasomatic differences that can be related
to initial host rock composition. Results also illustrate
distinct alteration and metasomatic similarities despite
probably different hydrothermal temperatures. This
comparison demonstrates that lithogeochemical exploration
exploiting patterns associated with hydrothermal alteration
zones about massive sulphide mineralization must be
undertaken with careful consideration of host rock
compositions and hydrothermal conditions that affected
the host rocks.

Lecture #3: This detailed talk contrasts the lithogeochemistry
of relatively unaltered granitoid rocks with different magmatic
affinities. This talk illustrates the use of new lithogeochemical
data analysis procedures, and is intended for an advanced
undergraduate/graduate audience with an economic geology
orientation.

MOLAR ELEMENT RATIO ANALYSIS OF GRANITOID
BATHOLITHS: INSIGHTS INTO MAGMATIC AND
ASSIMILATION PROCESSES THAT AFFECT EXPLORATION
STRATEGIES AND TACTICS

The South Mountain batholith, Nova Scotia, is a
Devonian, peraluminous granitoid and host to Sn (East
Kemptville) and other rare-metal deposits. The Guichon
Creek batholith, British Columbia, is a Jurassic, calc-alkalic
granitoid and host to a major porphyry Cu camp (Highland
Valley). Compositional variations within both of these
batholiths can be attributed to a variety of magmatic and
assimilation processes, both of which have contributed to
metal accumulation. Results from molar element ratio
investigations of the compositional controls in each of these
batholiths indicate that these controls are startlingly similar,
yet have lead to significantly different types of metal
accumulation. Understanding the nature and extent of these
processes allows development of geochemical parameters
that can be used to identify where exploration potential exists
in these batholiths. Geochemical parameters that can be
used to map fractionation, assimilation and hydrothermal
alteration have been identified in both batholiths, and
illustrate significant patterns with direct exploration
implications.

Lecture #2: A detailed talk: lithogeochemistry of
hydrothermally altered rocks is compared around two mineral
deposits with different genesis. This lecture illustrates the use
of new lithogeochemical data analysis procedures, and is
intended for an advanced undergraduate/graduate audience
with an economic geology orientation.

Lithogeochemistry: What You Discover Depends
On Where You Stand

Quantitative methods for evaluating rock chemistry
typically have involved examination of simple scatterplots
and the statistical evaluation of concentration data.
Unfortunately, some characteristics of the lithogeochemical
data make numerical evaluation in this way difficult, if not
statistically or philosophically invalid. Rock compositions sum
100%, and so are not independent. Furthermore, virtually
all geochemical processes are at least partially deterministic
(they follow a distinct and predictable pathway based on a
quest for equilibrium). As a result, geochemical data are not
random, and thus statistical treatment generally may not be
appropriate.

Modern alternative data analysis methods – molar
element ratio analysis (MER) – that consider rocks as simple
mixtures of minerals facilitate interpretation and provide
opportunities for more refined and in-depth conclusions.
These methods consider rock compositions on a molar basis
and thus allow establishment of a more direct relationship
between lithogeochemistry and mineralogy. Furthermore,
these methods are founded on simple geometric principles,
and employ hypothesis testing as a means to conclude
information about a rock’s composition. Because geometric
projections are possible, consequences of competing
hypotheses can be examined independently, making
geochemical complexities readily interpretable.
Several examples of MER analysis applied to datasets
affected by a range of geochemical processes (hydrothermal
alteration, diagenesis, igneous fractionation, etc.) illustrate
the advantages of approaching lithogeochemical data analysis
in this manner.

Lecture #1: An overview talk: general lithogeochemical data
evaluation methods are discussed which can be applied in a
variety of geological disciplines. This talk specifically avoids a
mineral exploration/deposit focus, and is intended for a general
undergraduate/graduate audience.

The 2003 Distinguished Lecturer is Dr. Cliff Stanley.
Abstracts for the available lecturers follow. For further
information or to request a visit, contact:
Dr. C.R. Stanley
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Association of Exploration
Geochemists
Distinguished Lecture Series

Number 118 Explore
FOCUS: Certified Reference Material Discussion

EXPLORE is a forum for the sharing and dissemination of geochemical ideas, techniques and data that may not be fully developed or may be controversial. Publications in EXPLORE need not go through the thorough peer review that occurs with the GEEA. This less conservative approach to sharing geochemical issues should result in an active and vigorous dialog between the geochemists within the AEG, many of whom now have fairly established concepts of how geochemical surveys or geochemical processes should operate.

The recent incorporation of quasi-governmental rules that govern the quality of geological data collection and interpretation has spawned a new awakening to the importance of sampling and analyses in the geological (but perhaps not the environmental) community as a whole. I am seeing most Canadian mineral exploration companies addressing quality control issues that were not even recognized as issues prior to 1997. This awareness has, in turn, created many questions as to the appropriate application of in-field quality control samples.

For instance, a recent issue of EXPLORE contained an article by Lynda Bloom and Maureen Leaver (Number 115, p.3) that made the astonishing statement that the 95% confidence limit quoted on the certificate and bottle of a Canmet Certified Reference Material (CRM) “is not applicable for measuring the acceptability of a single analytical determination. Canmet is not alone in using that particular method of calculating confidence limits. One must ask the question therefore, “Why do organizations that manufacture and certify CRM’s insist on characterizing the material with a statistical parameter that is not useful to the client?” Lynda Bloom, with Maureen Leaver and Paul Hamlyn, provide a note addressing this question. The next issue will contain further discussion concerning Standard Reference Materials; additional submissions in this regard are welcomed.

On the geochemical process front, I continue to beat the hydrogen horse into at least a canter with the theoretical background that suggests that not many ions other than $\text{H}^+$ can move through appreciable thickness of cover and present some examples from actual exploration programs. I hope many of my colleagues enjoy these short communications and respond to EXPLORE with sharp wits and enthusiasm, for that is how progress is really made.

Barry W. Sme, Associate Editor

Barry Sme asked me to contact groups that prepare reference materials and answer the question “Why do organizations that manufacture and certify Certified Reference Material (CRM) insist on characterizing the material with a statistical parameter that is not useful to the client?”

My opinion has been that suppliers are demonstrating that their product is homogeneous and suitable for use as a reference material. Organizations such as CANMET (the well-respected Canadian government supplier) provide a range of statistics that can be used to assess laboratory performance but these are only available in an accompanying report. Although purchasers are advised when purchasing the materials, not everyone understands the implications or reads the fine print.

Is the mining industry alone in this situation? Maureen Leaver, of CANMET, forwarded an article titled “Non-use and misinterpretation of CRMs. Can the situation be improved?” (Lars Jorhem, 1998. Fresenius J. Anal. Chem. 360: 370-373). Jorhem surveyed the use of CRMs in the food industry and the following are extracts from his paper.

“When an analyst purchases a certified reference material (CRM) for use in the laboratory to check the quality of the results, he/she gets one or several bottles of the CRM, plus a certificate and sometimes a report. The certificate is usually very elaborate on the number of participants in the certification procedure, the different techniques used and the statistical evaluation of the certified intervals. Therof, however, a curious lack of information on how to use the CRM...None of the major producers of CRMs, however, have any information in the report/certificate on how the user should interpret the results from the analysis of the materials... Why not just proceed as usual and compare the results with the certified intervals? This cannot be recommended for several reasons

- It is not a statistically validated procedure, although it has developed into a de facto norm.
- The result of this comparison provides the user with little/no information about the analytical performance.
- When the certified interval is something else than the 95% CI [confidence limit] or 95/95% TL [tolerance limit] it is difficult for the user to interpret what it represents.
- The 95% CI is good for characterization purposes, but not for evaluation of results.
- It can be paradoxical in the evaluation.
- The CI (unadjusted) is dependent on the number of results: the more results, the narrower the interval becomes. When based on more than six results the 95% CI is narrower than the SD [standard deviation]."

Jorhem proceeds to give an example where results for 18 laboratories (using ICP, FAAS and INAA techniques) are all included in calculation of the 95% CI but in retrospect the results for three laboratories would all be regarded as unacceptable. Jorhem continues

"How can results that are perfectly good for the characterization of the CRM later be regarded as not acceptable? Simply because the 95% CI is well suited for characterization purposes, but highly unsuitable for evaluation of the results. The above-mentioned shortcomings strongly indicate that there is a need to develop procedures to make CRMs more useful to the customers.

Suggestions for improvement of the current situation

- The producers agree on a common model for presentation of the certified interval. This would greatly simplify the comparison with the results found.
- The producers provide the consumers with the information needed for an acceptable evaluation i.e. the certificates need to contain more information.
Certified Reference Material Discussion continued from page 9

- The guideline producing bodies [ASTM and ISO] cooperate with producers and users to establish evaluation procedures that are relevant and easy to use...[and take] several questions into account.
- What is the permissible range for laboratory means accounting for both between and within laboratory variation?
- What is the permissible range for the user’s individual results?
- What is the permissible range for the user’s means when the RM is used repeatedly, accounting only for within-laboratory variation?
- The producers start a dialogue with the users. It is the needs of the users that should be the foundation of the producer’s existence.
- Scientific journals should be encouraged not to accept papers that lack proper validation of results (e.g. by use of CRMs).”

I was amazed to find that Jorhem laid out exactly the issues that we wish to address in this Explore ‘dialogue’ and I decided to quote his paper as a reflection of the universality of the problem. A total of eight reference material suppliers were contacted in the U.S., Canada, South Africa and Australia. Responses were received from several sources.

Neil Fuge of CDN Resource Labs, a relatively recent addition to the Canadian market wrote “CDN agrees with your position [as reviewed in an article by Lynda Bloom and Maureen Leaver (EXPLORE Number 115, p.3)]. We do, and always have, reported the “between lab” standard deviation and accompanying 95% confidence interval. We find it disturbing that other standard manufacturers do not.”

Peter Hayes, Geostats, provided the following comment “Geostats is unique in the way values are assigned to reference materials in that a six-monthly survey of laboratories is utilized to test our products. Consequently, Geostats values are the result of analyses from up to 100 separate laboratories. Outlier values are removed and a core data-set of analyses remains available to clients. We give mean values and standard deviations on our products that should be reproducible by any laboratory in the world – on a single assay. We know that the product is much better than the tolerances quoted but this is generally irrelevant to the monitoring requirements of our clients. We did a comparison of real values generated on our standards and those on CANMET standards last year and were surprised to see that some of our products, if reported in the same manner, had tighter control limits than CANMET. CANMET, however, have a continuity of products second to none and seem to be able to provide the same materials for decades.”

Maureen Leaver (CANMET), Paul Hamlyn (Ore Research) and Malcolm Smith (Rocklabs) all submitted longer responses and these are published here in their entirety. The first word goes to Maureen Leaver as she is writing on behalf of CANMET, an organization which has the longest history of providing standards and perhaps set the ‘standard’.

I hope that this issue of EXPLORE helps us move towards a systematic approach to evaluating results for reference materials. My earlier quotes from Jorhem (1998) are indicative that the problem persists in several industries. As Jorhem is discussing practices in the food industry, I certainly hope that they managed to resolve the issue since this is a reflection on the quality of food that we consume.

We hope to develop acceptable practices on the uses of CRMs to improve our science and the economics of our mining projects. We would welcome further comments and submissions on this subject.

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Answers to Some Questions on Confidence Limits

1. How did the practice evolve of labeling standards with the 95% C.I.?

CCRMP quotes the certified value followed by the 95% confidence interval in accordance with ISO Guide 31 which deals with the contents of certificates, certification reports and labels of reference materials. This Guide is one of many developed by ISO/REMCO. The mandate of REMCO, the Council Committee on Reference Materials of the International Organization for Standardization, is to carry out and encourage a broad international effort for the harmonization, production and application of certified reference materials (CRMs).

ISO/REMCO has been in existence since the 1970’s. This group is comprised of the producers of reference materials world wide from all sorts of domains e.g. food, manufactured products and naturally occurring materials, who develop these guides to govern all aspects of processing, certification, statistics etc. ISO/REMCO is presently examining the certification of the producers of reference materials.

2. How can we make it easier for users to have access to the necessary statistics?

In the past CCRMP has distributed a 5 page brochure with examples on the assessment of accuracy and precision of the results obtained with reference materials with each order, and when questions on this topic are raised by clients. This topic has also been presented at several conferences internationally. This material is available upon request. Further work is required.

3. Is it a case of caveat emptor or does the supplier have a responsibility to help the buyer use the materials properly?

The role of the producer of the reference material to help the buyer was identified as a responsibility of the producer of reference materials at a recent ISO/REMCO meeting.

continued on Page 11
4. How has the application of inappropriate limits affected laboratories?

I have heard of much grief from analysts who have encountered this problem. In fact, the brochure mentioned in the response to question 2 was developed in 1997 as a result of almost weekly enquiries to CCRMP on this topic.

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Recommendations for the Preparation of CRM's

1. The Confidence Interval
The 95% Confidence Interval alone is an unsatisfactory measure of the quality of a Certified Reference Material (CRM). It is a measure of the effectiveness of the consensus testing and hence provides the user with an estimate of the degree of certainty of the Recommended Value. The magnitude of the confidence interval is inversely proportional to both the number of participating laboratories and the consensus in mean values of participating laboratories. Because measurement error is generally the major influence affecting consensus, the Confidence Interval bears little relationship to the physical attributes (in particular homogeneity) of the RM. This can be readily demonstrated by an interlaboratory certification program in which each participant receives a set of 4 to 6 subsamples considered representative of the entire batch of RM. If the variance within each laboratory dataset is low (i.e. good repeatability is evident) then we can be reasonably confident that the disparity amongst laboratory dataset means is primarily due to analytical bias.

2. Anatomy of a gold CRM
Consider a 1000 kg batch of a gold ore RM packaged into 1 kg jars. Two types of inhomogeneity may be present which will be referred to here as long and short wavelength. Long wavelength variation (Fig. 1a) is the result of subtle changes in gold content in successive jars of the RM. It is the most insidious of homogeneity problems as it can only be identified by the end user after exhaustive and costly investigation. It is generally the result of poor blending or handling procedures. Short wavelength variation (Fig. 1b) is the most common problem encountered in substandard gold RM’s and is manifested by poor repeatability in within-unit replicate assays. It can be caused by a number of factors such as lack of intimate blending, or presence of coarse gold (the nugget effect). Figure 1c illustrates the geochemist’s worst nightmare – the presence of both long and short wavelength inhomogeneity.

These examples serve to highlight the importance of homogeneity in a gold standard and the need to quantitatively document this property to the satisfaction of the user.

![Figure 1a. Gradual (long wavelength) drift in gold content of successively packaged 1kg units.](image)

![Figure 1b. Illustration of within-unit (short wavelength) inhomogeneity.](image)

![Figure 1c. Combined short and long wavelength inhomogeneity.](image)

3. Measures of homogeneity

Analysis of Variance. The nested ANOVA (ISO, 1985) is designed to establish that the between-unit homogeneity of an RM is statistically no poorer than the within-unit homogeneity. Each lab receives at least two subsamples from each of two or more units in the RM batch and the within- and between-unit variances of each lab are compared. It is a very effective means of demonstrating the absence of long wavelength variability in an RM but, being a comparative test, provides no information on absolute homogeneity. It instead provides an assurance that all units are of similar pedigree, be that good, bad or indifferent.

Reduced analytical subsample. In 1994 Ore Research & Exploration (ORE) introduced a method of quantifying the absolute homogeneity in a gold RM by employing a reduced analytical subsample weight. Instrumental neutron activation analysis (INAA) was chosen as the most appropriate technique owing to its good analytical precision. Generally 15-25 analyses are carried out using an analytical subsample weight of 0.5 gm. The objective is to employ a sufficiently reduced subsample weight in a series of determinations by the same method so that measurement error becomes negligible in comparison to sampling error. The corresponding standard deviation at 50g subsample weight can then be determined from the observed standard deviation of the 0.5g data using the known relationship between the two parameters (Kleen, 1967). A 95% Tolerance Interval is then determined from this parameter according to ISO recommendations (ISO 1975).

Figure 2 illustrates the results of homogeneity testing
by this method of 64 custom SRM's and off-the-shelf CRM's in the range 45 to 9,190 ppb Au. For gold contents above 200 ppb, the 95% Tolerance Intervals thus obtained are considered an excellent measure of homogeneity. At concentrations below this, the lower limit of detection is approached and analytical error contributes a substantial component of the observed standard deviation. The Tolerances Intervals calculated for these RM's are therefore considered a conservative estimate of homogeneity. All gold RM's prepared by ORE are tested in this way and 95% Tolerance Intervals are included along with Recommended Values and 95% Confidence Intervals in Certificates of Analysis.

![Figure 2. Relative standard deviations of means of replicate 0.5 gm INAA analyses for various RM's (Note: plot includes four < 100ppb Au RM's analysed using 1 gm subsample weights).](image)

4. Essentials of reliable CRMs
   a) The RM should be prepared from natural matrices with compositions matching as closely as possible the samples being analysed.
   b) The certification should incorporate a nested ANOVA program to ensure the absence of long wavelength variance. This imposes the requirement that each lab participating in a certification program analyse a minimum of four separately-packaged subsamples of the RM.
   c) The Certificate of Analysis should include a 95% Tolerance Interval obtained by the reduced subsample method outlined above. This statistic provides the end user with a reliable and quantitative measure of an RM's homogeneity.
   d) The 95% Tolerance Interval should be sufficiently narrow such that the sampling error pertaining to homogeneity is negligible in comparison to measurement error. The variance observed in a series of analyses of an RM by the same laboratory in the same batch should be a quantitative measure of that laboratory's precision.
   e) The 95% Confidence Interval should be sufficiently narrow to reflect a high degree of certainty in the Recommended Value.

References


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Response to comments about Reference Materials

The 95% confidence interval quoted by Reference Material producers is a characteristic of the Reference Material itself. It is a statement of the certainty that the producer has in the accuracy of the value that has been assigned to the Reference Material. It is not a measure of what any particular laboratory should obtain on a single analysis.

Another very important property of a Reference Material is its homogeneity. This is usually quoted in terms of its standard deviation or coefficient of variation (standard deviation expressed as a percentage of its assigned value). This property indicates how variable the results will be when different samples of the Reference Material are analysed by exactly the same procedure. The confidence interval is thus a statement of accuracy and the standard deviation (or coefficient of variation) is a statement of homogeneity: - two different and not necessarily related properties.

The results obtained by repeated analysis of a Reference Material by a user laboratory is another issue again. The repeated analysis of a Reference Material (RM) by a user laboratory will indicate whether that laboratory has a bias in its method and also how variable the individual results are (measured by standard deviation). Thus the RM is used to determine what the laboratory actually achieves, not what it should achieve. The average (mean? median?) of a very long series of results produced by the user laboratory should fall within the 95 % confidence interval quoted by the RM producer. If it is significantly outside the confidence interval then the laboratory has a bias. The user laboratory results can also be used to measure the reproducibility of its analytical method by calculating the standard deviation (coefficient of variation). If results are accumulated over time the results will reflect variations caused by different operators, calibration standards, reagents, pipettors etc. For these figures to be valid the homogeneity of the RM itself must be less than the standard deviation of the method used. For example if the coefficient of variation of the analytical method used by the laboratory is 4 % then the homogeneity of RM must be significantly less than this for it to be of any value in this regard. The homogeneity of the RM is determined by the producer in a separate homogeneity test and should be less than the coefficient of variation obtained in the round robin consensus test that is used to assign the value and 95% confidence interval.
Certified Reference Material Discussion continued from page 12

Recommendations for Using Reference Materials

We agree with the information provided in the well-written article by Lynda Bloom and Maureen Leaver. However the article does serve to highlight the difficulty in drawing conclusions about a laboratory's performance from just one or two analyses of an RM (unless, of course, the results obtained are widely different from the assigned value). We recommend that an RM is included in every batch of samples analysed. In this way the user laboratory can quickly gain information about its performance and build up a pattern of "normal" results. If an unusual RM result is obtained, an investigation should be carried out immediately. This is important because the problem that gave rise to the unusual result is also likely to have occurred with the accompanying samples. It is therefore essential that the RM is utterly dependable. It is pointless to use an RM if, when an unusual result is obtained, the likely cause is blamed on the quality of the RM. Excuses we have heard for in-house "standards" in such situations are: "it has absorbed moisture", "it is not homogeneous", "segregation has occurred".

Reliability and economic price make it desirable to use professionally prepared RMs on an every-batch basis.

Plotting the RM results on a control chart makes it easy to see when analytical problems are occurring. Indicator lines drawn at one, two and three standard deviation intervals from the average (mean? median?) help interpret the results. The average and standard deviation should be calculated from the user laboratory results and not from any data supplied in the RM certificate. Any trends from the user laboratory norm can then be easily identified. One set of patterns that are often taken as warning signals are:

- A single result more than three standard deviations from the average.
- Two out of three consecutive results more than two standard deviations from the average.
- Four out of five consecutive results more than one standard deviation from the average.
- Seven consecutive results that are all above or below the average.
- Ten out of 11 consecutive results that are all above or below the average.
- Seven consecutive results that are all increasing or decreasing.

Summary

The Reference Material producer provides data that reflect the properties of the product. A Reference Material that has a narrow 95% confidence interval and a low coefficient of variation as determined by an appropriate homogeneity test can be used by laboratories to provide data on the accuracy and reproducibility of their analytical procedures. It is not up to the reference material producer to declare what levels of accuracy or reproducibility the user laboratories should obtain, as laboratories will perform differently.

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Selected Geochemistry Web Sites of Interest

The following column highlights some of the favorite geochemical and technical web-sites of our members. If we have missed your favorite technical sites and would like to contribute, please send site addresses with a brief description along to the editor, and we will include them in our list. This list is of course provided for information only; AEG and the editors do not endorse nor specifically recommend any of the service providers.

Geochemistry Link Sites

www.aeg.org
Association of Exploration Geochemists
http://www.geo.cornell.edu/geology/classes/
Geochemweblinks.HTML
Cornell University

Geochemical Standards
www.rocklabs.com
Reference materials for gold assaying QA/QC.
www.nrccan.gc.ca/mms/canmet-mtb/crrnp/
- This is the Canadian Certified Reference Materials Project home page. There is a price list and summary information on CANMET standards here.
www.iaea.org/programmes/nahunet/e4/nmm/index.htm
- This is the International Atomic Energy Agency's database of natural reference materials home page. Here, you can browse by periodic table to find CRM's from around the world that are certified for each element. It is fairly exhaustive.
- The NIST also has a page covering standard reference materials.
www.oreresearch.com
Ore Research & Exploration Pty Ltd (Commercially available geochemical standards).
http://geoanalyst.org/ Reference Standards

Geochemical Laboratories
www.actlabs.com ACTLabs Laboratory
www.acmelab.com ACME Laboratories
www.alschemex.com ALS-Chemex Laboratories
www.sgs.ca SGS Labs
transport (another form of diffusion), or by true diffusion along overburden grain boundaries.

If ions move by hydromorphic processes, (i.e. ions dissolved in water), then a careful application of "normal" geochemical methods should detect responses to mineralization where the water meets the surface boundary. More likely, any ore-forming elements in interstitial soil or overburden waters would be in the form of colloids or adsorbed on soil grain surfaces, and would be transported by diffusion as well.

The theoretical transport velocities of cations due to diffusion through clay and calcareous soils was investigated by Smee, (1983a), and validated by radioisotopic measurements (Smee, 1983b). It was shown that concentration profiles can be calculated for the soil and boundary conditions important to applied geochemists by the relationship:

$$C_i(x,t) = C_{i_0} \exp \{-k_i/S \cdot 2C_i \exp \left[-(np/t)^2 D_i \cdot t \right] \sin((np/t) x) \}$$  \hspace{1cm} (1)

Where:

- $C_{i_0}$ is the concentration of diffusing substance at distance $x$ (cm) from the interface and time $t$ (s) from the start of diffusion, in M cm$^{-3}$.
- $C_i$ is the initial concentration of diffusing ion, M cm$^{-3}$.
- $D_i$ is the effective diffusion coefficient, which must be determined by taking into account the media tortuosity, moisture content, ion stability in the Eh-pH regime, and partition coefficient between particles and interstitial water for the ion in question and the soil substrate.

Equation 1 can be used to calculate concentration profiles for any initial condition of $C_i$ and for any time, $t$ for chelatable cations such as Zn$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, and Fe$^{3+}$. Chelatable ions become fixed at the upper boundary by some process (adsorption, chelation, precipitation) and change the concentration gradient as diffusion progresses.

Diffusing ions that are not chelatable or otherwise rendered immobile in the near surface soils such as H$^+$, K$^+$, and Na$^+$, require a different boundary definition:

$$C_{i_b} = C_i - 4C/p \cdot \exp \{-2/\alpha (1/2n + 1) \exp [-((2n + 1)^2 / D_{i_b} \cdot (p/4)^2 \cdot t)] \}$$  \hspace{1cm} (2)

However, more important to applied geochemists is the total mass per unit area (M/A) of diffusing ion that will pass into an organic or other soil horizon over a length of time, t, at a distance l, from the initial boundary. This expansion is given by Crank (1975) as:

$$M/A = D_i C_i /l^2 - D_i /l^2 \cdot t \exp [-((np/t)^2 D_i t)]$$  \hspace{1cm} (3)

Equation 3 was used by Smee (1983a) for a number of ions in the glaciolacustrine clay belt of Canada using the following conditions for mass transport:

<table>
<thead>
<tr>
<th>Ion</th>
<th>C$_i$ M cm$^{-3}$</th>
<th>D$_i$ cm$^{2}$ s$^{-1}$</th>
<th>t s</th>
<th>l cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$^{2+}$</td>
<td>3.3 x 10$^{-8}$</td>
<td>6.3 x 10$^{-8}$</td>
<td>2.5 x 10$^{-11}$</td>
<td>100, 250, 500</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>3.0 x 10$^{-6}$</td>
<td>5.0 x 10$^{-6}$</td>
<td>2.5 x 10$^{-11}$</td>
<td>100, 250, 500</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>1.0 x 10$^{-8}$</td>
<td>1.0 x 10$^{-8}$</td>
<td>2.5 x 10$^{-11}$</td>
<td>100, 250, 500</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>9.0 x 10$^{-8}$</td>
<td>3.0 x 10$^{-8}$</td>
<td>2.5 x 10$^{-11}$</td>
<td>100, 250, 500</td>
</tr>
<tr>
<td>H$^+$</td>
<td>1.0 x 10$^{-3}$</td>
<td>1.8 x 10$^{-3}$</td>
<td>2.5 x 10$^{-11}$</td>
<td>100, 250, 500</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.5 x 10$^{-4}$</td>
<td>1.0 x 10$^{-4}$</td>
<td>2.5 x 10$^{-11}$</td>
<td>100, 250, 500</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>2.0 x 10$^{-4}$</td>
<td>6.0 x 10$^{-4}$</td>
<td>2.5 x 10$^{-11}$</td>
<td>100, 250, 500</td>
</tr>
</tbody>
</table>

The time t is 8000 years, an estimate of the period for a sulphide body to undergo oxidation beneath a till and clay cover since the last Canadian glaciation. C$_i$ concentrations were actually measured in clays and waters from the base of the overburden. D$_i$ values (with the exception of Zn, which was actually measured using a radioisotope, Zn$^{60}$) were obtained from various publications, usually in the soil physics, plant nutrition, or radioactive waste disposal disciplines. The D$_i$ for H$^+$ is nearly 300 times higher than for the ore-forming cations. The boundary length l varies from 100 to 500 cm and is the distance to the upper boundary (surface) from the lower boundary.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Thickness, cm</th>
<th>M/A in M cm$^{-2}$</th>
<th>C$_i$ in soil horizon$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$^{2+}$</td>
<td>100</td>
<td>1.1 x 10$^{-11}$</td>
<td>0.72 ppm</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>250</td>
<td>&lt;1.0 x 10$^{-10}$</td>
<td>nil</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>250</td>
<td>&lt;1.0 x 10$^{-10}$</td>
<td>nil</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>100</td>
<td>&lt;1.0 x 10$^{-10}$</td>
<td>nil</td>
</tr>
<tr>
<td>H$^+$</td>
<td>100</td>
<td>4.3 x 10$^{-2}$</td>
<td>pH = 3.37</td>
</tr>
<tr>
<td>200</td>
<td>1.4 x 10$^{-3}$</td>
<td>pH = 3.85</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>2.4 x 10$^{-4}$</td>
<td>pH = 4.62</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>100</td>
<td>1.3 x 10$^{-3}$</td>
<td>0.51 %</td>
</tr>
<tr>
<td>250</td>
<td>&lt;9.0 x 10$^{-3}$</td>
<td>nil</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>100</td>
<td>5.8 x 10$^{-4}$</td>
<td>0.13 %</td>
</tr>
<tr>
<td>250</td>
<td>&lt;1.0 x 10$^{-3}$</td>
<td>nil</td>
<td></td>
</tr>
</tbody>
</table>

The calculations show that only H$^+$ can move through anything more than 100 cm of clay cover in a mass per unit area that could be measured by any form of SWE or instrumentation. All other ore-forming cations occur in concentrations less than 1 x 10$^{-10}$ M cm$^{-2}$, much lower than what can be separated from normal background noise. This situation has not changed in the 20 years since this work was published, regardless of leach or analytical sensitivity (Smee, 1983b). Unless a form of transport other than diffusion is active (such as hydromorphic migration through porous soils, or mechanical transport) a direct anomaly formed from the target cations in the glaciolacustrine-covered areas will not be detected through more than 5 m of impervious cover. The target ions never make it to the surface at all.

Other parts of the world have their own geochemical challenges. Semi-arid to arid areas are usually highly alkaline and oxidized. Under these Eh-pH conditions, ore-forming cations are normally stable in the form of oxides and carbonates (hence oxide caps). The ore-forming cations move very little because D$_i$ is extremely small, even though time is large. Again, no direct geochemical response to mineralization should be expected in arid areas with appreciable exotic overburden cover.

The geochemical method that should be most

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1. The D$_i$ in soils can be 5 orders of magnitude less than the published D$_0$ in aqueous solutions. The D$_i$ values for the number of cations can be found in various soil science publications.
2. Assuming total fixation of cations in a 10 cm thick organic horizon of density 1 g/cc.
consistently successful, regardless of the environmental conditions, is one that seeks an indirect response to sulphide mineralization. An indirect geochemical response is a change in the distribution of major or trace elements at the overburden-surface boundary that is in response to another stimulus associated with the underlying mineralization. Examples of an indirect pattern have been published for years by many workers in both the mineral and petroleum exploration industries (Donovan (1974); Smee (1983a,b, 1997, 1998, 1999, 2001); Hamilton (1998), Hamilton et al., (2001b)).

A further form of response to buried or blind mineralization could be called a secondary indirect indicator. This is a pattern formed by base or precious metal cations that appear to be caused by their movement through overburden above or on the margins of mineralization. These patterns, which are often highlighted by SWE methods, are actually formed by the scavenging of available cations in the surface soil by precipitating pH sensitive cations. Positive responses in SWE Cu in soils, for instance, may correlate perfectly with a SWE/Hot Acid Fe, Mn, or Ca ratio. A regression of these two variables completely eliminates the Cu response. Thus many of the published successes of SWE methods are actually related to changes in pH in the surface soils.

This phenomenon is illustrated in Figures 1 and 2. The example in Figure 1 is from the Magusi River Cu-Zn massive sulphide deposit in Western Quebec, Canada. The sulphide horizon subcrops beneath 5-10 m of glaciolacustrine sediment and till. The SWE Cu, done by cold EDTA/AAS is ratioed against a hot aqua regia extraction to show that the Cu anomaly is not caused by a simple increase in total Cu. That ratio is then corrected for the total number of ion binding sites in the organic-rich soil by ratioing against organic C. The resulting pattern makes it appear that the SWE methods detected a clear double-peak Cu response from the margins of the sulphide body.

Figure 2 shows the result of taking the above response and regressing against a similar treatment for SWE Fe. If the Cu actually traveled through the clay to surface, there would be a residual Cu pattern above the sulphide. In fact, the Fe accounts for all the Cu, leaving no trace of Cu attributable to the upward migration of that element.

The model for the formation of at-surface indirect element anomalies such as Ca, Fe, Mg and Mn in response to a change in $H^+$ in Canadian Shield conditions was developed by Smee (1983a,b) and confirmed by Hamilton et al. (2001b). Whether the geochemical gradient in overburden is caused principally by a change in Eh or pH is irrelevant to the method of transport of the resulting ionic products. All products must move by some form of diffusion and are thus governed by diffusion principles.

Smee (1997, 1998) published a similar model of ion transport and indirect anomaly formation for arid conditions which showed the added possibility of gaseous transport in dry overburden. The $D_e$ for gases traveling through a dry porous medium is usually much larger than for ionic species in water, thus producing the interesting possibility of indirect geochemical anomalies that have formed through a significant thickness of cover.

All geochemical contributors attribute these indirect geochemical patterns to changes in Eh-pH conditions induced by the oxidation of the mineralization, or reduction of the overlying rock by hydrocarbons. Workers recognize...
that a reproducible measurement of Eh (Oxidation-Reduction Potential ORP) is a difficult and time consuming undertaking (Smee, 1983a; Hamilton et al., 2001a). As well, workers recognize that an in-field pH measurement is simple, fast, reproducible and cost effective, and produces similar or clearer responses to mineralization than does a measurement of Eh or ORP.

Smee (1983a) suggested that a simple field pH measurement, that reveals patterns in the pH sensitive cations such as Ca++, would be an effective indirect geochemical exploration tool in the Canadian Shield. Smee (1998, 1999) further illustrated that field pH measurements could be a viable direct and indirect geochemical tool for arid terrain using an example from Nevada. A pH meter and a source of distilled water are all that is necessary to locate sulphide mineralization.

A few companies began testing the concept either in the field or by measuring pH routinely in the laboratory. Some of these results have been released with permission.

Soil H+ profiles over gold-bearing structures, Chile

The Atacama desert of northern Chile is one of most arid places in the world. Much of the terrain is overlain with salt deposits consisting of calcite, gypsum, nitrates and halogen salts of various compositions. These salt deposits may form over shallow colluvial cover or valley-filled alluvium that may reach several hundreds of metres thickness. The surficial aridosols are almost universally alkaline and may exceed a pH of 10 in some instances. As previously mentioned, most base metal cations are stable in these conditions, so the D, for all of these cations is extremely small. It is unlikely that base metal cations are transported through this alkaline cover in any concentration that could be detected by soil sampling.

In this environment, like the Nevada example, a portable pH meter and some water may be all that is required to detect the products (both direct and indirect) of buried or blind oxidizing sulphides. The direct indicator would be a change in soil pH, whilst the indirect indicator would be a change in concentration of the pH sensitive cations such as Ca, Fe and Mn.

Experience has shown that the latter style of anomaly is not easily reproduced in the Atacama desert because the presence of gypsum masks the possible movement of calcite, and the formation of gypsum is not sensitive to pH conditions. The amount of Ca in the form of calcite is not easily separated from that of Ca that is in the form of gypsum, when only performing multi-element ICP-ES or MS analyses. Attempts at screening ICP analyses by using S and ratios with Ca have not been successful.

A series of field tests have been carried out using a portable pH meter and distilled water with soils collected on traverses over known mineralized structures. Approximately a teaspoon of soil was mixed with 50 ml of distilled water for 2 minutes, before reading the pH, as shown in Plate 1.

Results were converted to moles H+ to remove the log scale before plotting. A single traverse over a buried mineralized structure is shown in Figure 3. Soil samples were spaced at 50 m over the surface projection of the mineralization, and 100 m away from the mineralization. The H+ clearly shows the position of the sulphide mineralization as a double-peak response. There is a 10-fold change in H+ concentration compared to background, however there is no discernable visible change in the surface soil textures or mineral components.

The relationship of soil Ca to soil Cu Oyu Tolgoi, Mongolia

The Oyu Tolgoi (Turquoise Hill) project is located within the South Gobi desert in Mongolia. The climate is classified as semi-arid with low shrubs and small trees supported by meager precipitation. Soils are typical aridosols featuring a ubiquitous calcite-enriched horizon near surface. This caliche is not indurated into a hard layer or crust, but can be easily outlined with a few drops of dilute HCl. Mineralization is still being discovered, and is taking the form of multiple disseminated copper-gold-molybdenum bodies within or around intrusive rocks. Sulphide mineralization is highly weathered and forms both oxide and secondary sulphide layers above or in proximity to the primary sulphide mineralization.

The presence of copper in this area has been known since the bronze age. The initial modern exploration was

Plate 1: Field Portable pH meter measuring surface soil pH, Atacama desert.
performed by BHP Minerals in the mid to late 1990s. As part of that exploration, BHP conducted a soil sampling orientation program over then known mineralization. Samples were analyzed for pH, strong acid soluble elements by ICP-ES, and most of the available SWE methods. All of the extraction methods reveal the sub-cropping mineralization as shown by copper in Figure 4.

![Figure 4](image_url)

**Figure 4:** Aqua regia soluble copper in soils ppm, Oyu Tolgoi, Mongolia. Survey clearly reveals the main mineralization. Area to the east is covered by sand and overburden.

A commercial laboratory did the soil pH measurements over a period of three years. The pH analytical method either varied from year to year or the internal controls were not stable over the sampling period. This produced pH data that is obviously influenced by sampling episode, and resulted in "along-line" patterns that do not represent geological features. Nonetheless, soil pH (when converted to Moles H+) is useful in showing northeast and northwest striking structures in the overburden-covered eastern areas. This area was sampled and analyzed in one campaign. Curvilinear responses on the edges of known mineralization occur in the central portion of the grids as shown in Figure 5.

Copper contours superimposed on a 3D relief image of aqua regia soluble calcium in soils are shown in Figure 6 (page 1). Although the calcium shows a great deal of noise in other portions of the sampled area, it is absent from soils over the main areas of mineralization as shown by the copper. A weak two-line copper response in the northern portion of the grid is also devoid of calcium. This is the area of the newly discovered North Oyu mineralization.

There is therefore both a direct and indirect indication of mineralization in the aqua regia multi-element information. A single aqua regia and ICP-ES analyses would give both indications of mineralization for a nominal cost of analyses. A field measurement of soil pH, or a well-controlled laboratory measurement should produce information helpful in locating oxidizing sulphides and water-bearing structures.

**Conclusions**

The use of a simple pH measurement on soils in the field can produce both direct and indirect indications of sulphide mineralization. The method is not specific to any deposit type; only the presence of sulphides is required. More importantly, the distribution patterns shown by H\(^+\) and the pH sensitive elements such as Ca, Fe, Mn, and Mg indicate that a specific mode of element transport is operational through many types of soil and in many climatic conditions. Over the past 25 years I have observed similar patterns of element distribution from the high arctic through the boreal forests and the Atacama desert. This is a clear indication that a specific transport mechanism is operational and should be examined in detail to fully understand the geochemical methods that are useful when searching for blind deposits.

The data required to understand these mechanisms are already available, but not in the applied geochemical field. Soil and forestry physicists, nuclear waste management scientists, and other experts in ion movement have an existing bank of data and experience available for the having. Several years ago I put forward a proposal to a Canadian mineral research organization to hire an ion migration specialist from outside the field of applied geochemistry who would compile...
Geochemical Process Debate
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the required data from the various sources. This proposal was rejected out-of-hand as not being relevant to solving the problems of exploration for blind mineral deposits. Now that many hundreds of thousands of dollars have been spent, and we appear to be where we were twenty-five years ago, I suggest this idea be revisited by an applied geochemical research organization. If we as a group of applied geochemists are to survive, we must broaden our knowledge of sister fields. This cross-fertilization of ideas will, I believe, give the impetus we require to make significant advances in searching for mineral deposits.

Acknowledgements
I would like to express my appreciation to Dave Heberlein of Barrick Gold and Charles Forster of Ivanhoe Mines for technical and moral support and for permission to present the data from the Atacama desert, Chile and Oyu Tolgoi, Mongolia respectively.

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References

Mann, A.W., Birrell, R.D., Mann, A.T., Humphreys, D.B., continued on Page 19
Geochemical Process Debate
continued from Page 18


New Members...

To All Voting Members:
Pursuant to Article Two of the Association’s ByLaw No.1, the names of the following candidates, who have been recommended for membership by the Admissions Committee, are submitted for your consideration. If you have any comments, favorable or unfavorable, on any candidate, you should send them in writing to the Secretary within 60 days of this notice. If no objections are received by that date, these candidates will be declared elected to membership. Please address comments to David B. Smith, Secretary AEG, USGS, Box 25046, MS 973, Denver, CO 80225, USA.

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Direct Geochemical, Denver, USA
Scott A Wood, Professor of Geochemistry,
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Robert G. Jackson
Consulting Geochemist

3D Zonation Modeling and Vectoring Methods to discover Blind Deposits
Survey Designs and Data Interpretation

Seeking new target possibilities through 3D visualization

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rgjackson@ctnis.com 775-777-3619


Smee, B.W., 1997. The formation of surficial geochemical pattern over buried epithermal gold deposits in desert environments. Results of a test of partial extraction techniques In Exploration 97 Symposium Volume, Toronto: 301-314.


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PAGE 19

Vancouver 1996
Technical Note

Atlas of Landscape Geochemical Models for Porphyry Copper, VMS and Gold Deposits in the Cordillera from Alaska to Nevada

Introduction

Today, a typical geochemical survey can generate many thousand items of field and analytical information so the geologist or geochemist often faces a daunting task when attempting to make full use of this large volume of information successfully. Fortunately, geochemical models can provide one strategy for dealing with this problem by providing a framework of basic principals upon which data for specific properties can then be interpreted. Geochemical exploration models (GEM's) simplify the information from numerous case histories by visually demonstrating the relationships between mineral deposits and their geochemical response. First proposed by Bradshaw (1974) for the Canadian Cordillera and Canadian Shield and later adapted by Kauranne (1976), Lovering and McCarthy (1978) and Butt and Smith (1980) for other parts of the world, the models have been displayed as a series of conceptual, three-dimensional diagrams.

Much more information has become available on topics such as selective extractions, lithogeochemistry, surficial geology since these papers where published and there is a need to update the earlier models. Ideally, these models should be presented as an Atlas providing a simple, visual aid to geochemical exploration for a variety of mineral deposits under a range of different environments. The original models generally did not distinguish between the geochemical response from one deposit type and another. It is now apparent that this is an over simplification. Hence, the approach of this current proposed compilation will focus on specific and diverse deposit types. A special issue of Geochemistry, Exploration, Environment and Analysis is planned for this Atlas.

A critical part of the Atlas is that every detail added to every GEM will be supported by field examples. This is a call for data and/or examples and/or papers to assist in compiling this Atlas and making it comprehensive.

The authors of this note will construct draft GEM's from all the data received which would be available for review, modification and approval by all participants. A meeting is planned in Vancouver during the British Columbia and Yukon Chamber of Mines Cordilleran Roundup Symposium in January 2003 to review progress towards developing draft GEM's. Volunteers to assist in this compilation are most welcome.

The GEM's in the proposed Atlas would be constructed from combinations of the three mineral deposit types, for each of the surficial environments and for each landscape (as long as sufficient data is available) identified in Table 1. Clearly, there could be a large number of GEM's based on these alone.

Table 1. GEM mineral deposit, surficial environment and landscapes categories

<table>
<thead>
<tr>
<th>Mineral Deposit</th>
<th>Surficial Deposit</th>
<th>Landscape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volcanogenic</td>
<td>Residual</td>
<td>Alpine (well drained, poorly drained, perm入ered)</td>
</tr>
<tr>
<td>Massive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphide (VMS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porphyry Copper-Molybdenum</td>
<td>Transported - local source (e.g. shallow till, colluvium)</td>
<td>Forest (coastal, boreal, well drained, poorly drained)</td>
</tr>
<tr>
<td>Gold (Epithermal vein, Carlin type)</td>
<td>Transported - remote source (e.g. alluvium, fluvio-glacial, lacustrine)</td>
<td>Dry forest - grassland Wetland (fen, raised bog) Desert</td>
</tr>
</tbody>
</table>

Each model will deal with all facets of geochemical exploration e.g. stream sediments and waters, lake sediments; various soil types ranging from well drained to bogs to deserts; lithogeochemistry; biogeochemistry, different size fractions and different chemical extractions. In Figure 1, the mineral deposits (with their multi-element signatures), surficial deposits and landscapes are shown three dimensionally. The various combinations of these (e.g. Au in residual soil alpine environment) will go to make up each individual GEM.

A draft example of a GEM for volcanogenic massive sulphide (VMS) mineralization in a glaciated part of southern British Columbia, Canada is given below based on limited existing information. When more data is available from other examples this GEM will be modified and expanded.

A provisional GEM for VMS mineralization in southern B.C.

Several diagrams are used to formulate a single geochemical exploration model. Broad, spatial, element variations are summarized on three-dimensional block diagrams whereas more detailed horizontal and vertical geochemical changes may be better demonstrated using cross sections and prisms. The diagrams are

continued on Page 21
purposely constructed with no scale. Geochemical anomaly size and contrast are variable, dependant on a number of features such as the extent of the mineralization at the bedrock surface, mechanical and chemical dispersion and overburden type. The models are designed to demonstrate geochemical relationships and dispersion processes in the near-surface environment that are independent of scale. However, anomaly dimensions can be predicted by linking these models to the supporting case histories gathered from geochemical case studies and orientation surveys. These predictions can be used when planning geochemical surveys to help to guide the selection of, for example: appropriate sample type, sampling density, and analytical method, and during interpretation to assist in determining the significance of anomalies. Likewise the primary geochemical haloes shown on the bedrock layer have no scale because the actual lithogeochemical anomaly size varies from deposit to deposit although the element signature may be similar.

An example of a GEM, constructed from a limited number of case histories, plus regional stream sediment geochemical survey data, is shown for VMS deposits in a glaciated area of moderate relief in southern B.C. (Figure 2). Bedrock geology and mineralization, surficial deposits (soil, till, etc.) and surface drainage are displayed three-dimensionally by a series of stacked, block diagrams. These diagrams are linked to geochemical landscape layers showing the observed geochemical expression of mineralization from the bedrock interface into the surficial deposits and vegetation. Ice-flow direction and the projected expression of mineralization at the bedrock surface onto the surficial layers are also shown on the diagrams.

Each type of mineral deposit has a distinctive element signature that may be reflected in the till, soil, vegetation, stream water and stream sediment geochemistry. Therefore, pathfinder element signatures are also shown on the GEM's because they can be very important in detecting mineralization as well as distinguishing between different sources of mineralized bedrock. In this example, the observed multi-element signature for the VMS deposit is As-Ag-Au-Ba-Bi-Cd-Cu-Hg-Pb-Se-Sb-Sn-Zn.

The direction of the glacial dispersal trains in till is displayed on the surficial geochemistry layer in Figure 2 with an indication of the relative strength of the till anomaly is shown by a shaded pattern. A Au-As-Ag-Ba-Cu-Pb-Zn-Hg-Sb-Se association in the till anomaly reflects mineralized bedrock transported down-ice from the VMS mineralization. The soil landscape layer combines the topography, drainage and predominant soil types (brunisolic, organic) typical of the bioclimate and landscape of the area surrounding the VMS deposit.

Patterns on the soil and sediment geochemistry layer indicate relative B-horizon soil and stream sediment anomaly size and contrast in a similar fashion to till. The relative strength of the geochemical response of mobile elements (e.g. Cu, Zn) and less mobile elements (e.g. Au, Pb) is also shown by patterns on the soil layer. The relationship between metal concentration in stream water and water pH is displayed on the water geochemistry layer. A Au-As-Cu-Pb tree-bark anomaly is indicated on the biogeochemical layer close to the surface projection of the VMS mineralization. Ideally, layers are only presented where there is supporting geochemical data.
The GEM reveals a number of geochemical anomaly characteristics related to VMS deposits in this environment.

1. Most of the ore forming pathfinder elements in the deposit are reflected in streams draining the mineralized area. However, less mobile elements such as Pb and Au may be weak or even absent in the stream.

2. Both the surficial geochemistry (till) and soil anomalies are larger in area than the mineralized sources due to down-ice smearing. Geochemically more mobile elements such as Cu and Zn may show a larger anomaly than less mobile elements.

3. Mobile elements (e.g., Cu, Zn) may form a seepage anomaly in organic soil at the break in slope. Seepage anomalies are typically stronger than those formed on well-drained soil.

4. Biogeochemistry is effective, but typically for a more limited number of elements.

5. Water sampling is less effective than sediment sampling as the range of anomalous elements is restricted to the mobile elements such as Cu and Zn.

Models Galore!
A challenge to constructing this GEM Atlas for a large region is to simplify the numerous possible combinations of surficial environment and geology into a manageable number of basic models. This can be achieved with a series of block diagrams that depict the main landscapes and bioclimatic zones and types of surficial deposit encountered along the Cordillera between Alaska and Nevada. The primary geochemical signature of porphyry copper-molybdenum, volcanogenic massive sulfide (VMS) and gold (vein) mineralization, representing important Cordilleran deposit types, has been shown schematically in Figure 1. The element signature for these deposit types is based on mineral deposit profiles previously published by Lefebure and Ray (1995), and Lefebure and Hoy (1996). For simplicity, there has been no attempt to propose models for the various sub classes of these deposit types (e.g., Cu-Au porphyry, Carlin type Au).

Ideally, models could be constructed for over seventy landscape-surficial-mineral deposit type combinations - a daunting prospect for the Atlas authors. In practice, the number of models is smaller because not all of the combinations of deposit type, landscape and surficial geology will be represented.

A second challenge making this Atlas is capturing all of the data needed to validate the models. To do this the authors invite Explore readers to contribute geochemical case histories from the western Canadian Cordillera and U.S.A. as soon as possible. Ideally the information should be provided under the following headings:

1) Name and location of survey area or mineral property (geographic and UTM).

2) Summary of Geology including alteration

3) Style of mineralization

4) (Potentially) Economic elements and associated elements

5) Topography, glacial deposits, soil types, vegetation

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Technical Note...  
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6) Geochemistry (including sample preparation and analytical method) in point form with maps, tables, diagrams (as appropriate) plus interpretation and conclusions.
   A. Lithogeochemistry
   B. Sediments and water
   C. Soil and overburden
   D. Plants
   E. Other (e.g. gas)

7) References. To avoid duplication, as far as possible refer to published references rather than including the data.

The authors would appreciate getting two copies of the printed article if case histories have already been published. Where authors are willing to provide unpublished data they are asked to submit it using the format shown above so the information can be presented in a compact manner and as much of the supporting data as possible can then be included in the special issue.

It is most important that people submit NEGATIVE EXAMPLES (i.e. a situation where geochemistry did not work) as well as positive examples, as it is only in a compilation of this type that such important data can be compared. (Remember the late Dr. Stan Hoffman’s invaluable “Pearl Harbour” file.)

Where “less-conventional” data are provided (e.g. results of different size fraction and/or selective extraction analysis, etc) it is most desirable that “conventional” data (e.g. minus 80 mesh, fraction-aqua regia extraction results) can also be provided for comparison.

Remember, this Atlas will be dynamic and models will be constantly improved as technology advances and more information becomes available. However, keep in mind that the underlying concept of the Atlas it to simplify complex geochemical data and enhance its practical application to exploration for mineral deposits.

REFERENCES


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CALENDAR OF EVENTS

International, national, and regional meetings of interest to colleagues working in exploration, environmental and other areas of applied geochemistry.

- February 24-26, 2003, Society for Mining, Metallurgy, and Exploration (SME) annual meeting, Cincinnati, OH. INFORMATION: SME (sme@smenet.org). SME, Meetings Dept., P.O. Box 277002, Littleton, CO 80127, 800-763-3132. SME (sme@smenet.org)

- March 8, 2003, Prospectors and Developers Association of Canada (PDAC), Short Course 2, Indicator mineral methods in mineral exploration, PDAC, 34 King Street East, Suite 900, Toronto, Ontario, M5C 2X8, CANADA, Tel: (416) 362 1969 Fax: (416) 362 0101, Email: info@pdac.ca, Website: www.pdac.ca

- March 12-14, 2003, Geological Society of America, Southcentral and Southeastern Section meeting, Memphis, TN. http://www.geosociety.org/meetings/


- April 7-11, 2003 EGS, AGU, and EUG Joint Assembly, Nice Conference Centre, Nice, France, by the EGS, AGU, EUG. (Meetings Department, 2000 Florida Avenue, NW, Washington, DC 20009 USA, Phone: +1-202-462-6900 FAX: +1-202-328-0566 EMail: meetinginfo@agu.org Web: http://www.copernicus.org/egsagueug/).

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Announcement

John Steven Cone Memorial Scholarship Fund

A scholarship fund has been established at the Colorado School of Mines in memory of Steve Cone (1941 – 2002), chemist, trusted advisor, gifted educator and close friend to many in the mining industry. The purpose of the scholarship is to support graduate research in exploration geochemistry and economic geology for students focused on a career in the mining industry.

Donations or inquiries should be directed to:

Colorado School of Mines Foundation
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1600 Arapahoe Street,
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Tel: 303-273-3140 Fax: 303-273-3165
Attention: C.G. Wenger, Director, Planned Giving (cwenger@mines.edu)

(Colorado School of Mines Foundation will issue receipts for tax purposes)
Calendar of Events

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May 7-9, 2003, Geological Society of America, Rocky Mountain Section meeting, Durango, CO.


April 14-17, 2003, Uranium Geochemistry, E-mail: Michel.Cuney@gr2r.ulp-nancy.fr


June 1-5, 2003, AMERICAN SOCIETY for SURFACE MINING and RECLAMATION (ASSMR) 19th National Meeting and Billings Land Reclamation, Billings, Montana. INFORMATION: Dennis Newman, dneuman@montana.edu, http://www.ca.uky.edu/assmr/Upcoming_Events.htm

June 8-10, 2003, 3rd Canadian Conference on Geotechnique and Natural Hazards, Edmonton, Alberta. INFORMATION: Corey R. Froese, c/o AMEC Earth & Environmental Limited, 4810 - 93 Street, Edmonton, Alberta, T6E 5M4, Fax (780) 435-8425, Email: corey.froese@amec.com.

June 9 – 11, 2003, Geoanalysis 2003, 5th International Conference on the Analysis of Geological and Environmental Materials, Rovaniemi, Finland. INFORMATION: Geological Survey of Finland, Geolaboratory/ Geoanalysis 2003, PO Box 1237, FIN-70211 Kuopio, Finland, Phone: +358 20 550 3670 Fax: +358 20 550 13, E-mail: Lars.Westerberg@gsf.fi Web: http://www.gsf.fi/geoanalysis2003/

July 12-18, 2003, 6th International Conference on Acid Rock Drainage (ICARD), Cairns, Australia; INFORMATION: Clive Bell, c.bell@mailbox.uq.edu.au or website http://www.ausimm.com.au/events/event_writeups/icard.asp


August 29 - September 3, 2003, 21st International Geochemical Symposium (IGES), North Atlantic Minerals Symposium (NAMS), Dublin, Ireland. Information: The Secretary, Eibhlin Doyle (e-mail eibhlin.doyle@gsi.ie), http://www.conferencepartners.ie/igesandnams2003.com


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Obolensky, United Institute of Geology, Russian Academy of Sciences, Novosibirsk, Russia 630090, Phone: 7-3832-33-30-28 FAX: 7-3832-35-27-92 EMail: obolensk@uigg.msc.ru Web: www.uigg.msc.ru/uigg/geology/admin/)

- September 22-26, 2003, 7th International Conference on Gas Geochemistry, Freiberg University - Conference hall “Alte Mensa”, FREIBERG, Sachsen, Germany, by the Freiberg University of Mining and Technology and Saxon Academy of Sciences. (Dr. Jens Heinicke, Saechs. Akademie der Wissenschaften /TU-BAF, B-v-Cotta Str. 4, Phone: +49-3731-392212 FAX: +49-3731-392212 EMail: heinicke@physik.tu-freiberg.de Web: http://www.copernicus.org/ICGG7)
- October, 2003, acquire 2003 Conference by McTech, coinciding with the Rugby World Cup, Perth WA.
- June 27-July 2, 2004, 11th International Symposium on Water-Rock Interaction, Saratoga Springs, New York, USA (Dr. Susan Brantley, Secretary General, Dept. of Geosciences, The Pennsylvania State University, 239 Deike Building, University Park PA USA 16802, Phone: 814-863-1739 FAX: 814-863-8724 Web: http://www.outreach.psu.edu/C&I/WRI/)
- Oct 10-15, 2004, SEG International Exposition & 74th Annual Meeting, Denver, Colorado, USA by the SEG. (Debbi Hyer, 8801 S. Yale, Tulsa OK 74137, Phone: (918) 497-5500 EMail: dhyer@seg.org Web: http://meeting.seg.org)

Please check this calendar before scheduling a meeting to avoid overlap problems. Let this column know of your events.

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ISEG 2003
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The 6th International Symposium on Environmental Geochemistry will follow on from previous symposia held every three years, the most recent being at Vail, Colorado, USA (1997) and Cape Town, South Africa (2000).

The Edinburgh Symposium under the chairmanship of John Farmer and involving the participation of AEG, BGS, IAGC, IM, IWGMG and SEGH, will bring together geochemists, environmental chemists, biologists, soil scientists, aquatic scientists and medical specialists. The main themes for the scientific programme will be:

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E-mail: Janet@in-conference.org.uk
Technical Note

Diamond Exploration Studies in Glaciated Terrain

Alberta Geological Survey scientists Roger Paulen, John Pawlowicz and Glen Prior continued their kimberlite and glacial dispersal studies in the Buffalo Head Hills kimberlite field of northern Alberta, Canada, this past summer. Fieldwork consisted of excavating trenches adjacent to and down-ice of the K4 kimberlite pipes, an auger drilling program and a regional till geochemical and kimberlite indicator mineral survey. The purpose of these activities was to document both indicator mineral and geochemical glacial dispersal patterns, to collect information on site-specific ice flow variations, and to determine the local Quaternary stratigraphy and till characteristics on the Buffalo Head Hills.

The glacial sediment thickness on the highlands was relatively thin, with several boreholes and one trench intersecting Cretaceous mudstone at depths less than 5 m. However, despite the thin overburden, the glacial stratigraphy was highly variable with multiple tills and intertill glacial sediments. The discovery of an older till will have to be taken into account when interpreting the dispersal pattern.

A large excavator was used to expose the complex glacial sediments that occur in the vicinity of the K4 kimberlite pipes.

Ice flow directional studies were conducted in the trenches at various depths to determine the history of site-specific ice flow at K4. Preliminary results indicate that the ice flow history in the Buffalo Head Hills was more variable than previously thought.

A detailed sedimentological study of the surface till was conducted in order to gain insight on the mineralogical and geochemical dispersal variations between till deposited by moving ice (lodgement) and till deposited by ice stagnation (ablation). Samples were collected to document any mineralogical and geochemical variation within the tills.

Relevant AGS publications:


Roger Paulen (glacial dispersal)
Alberta Geological Survey

John Pawlowicz (Quaternary stratigraphy)
Alberta Geological Survey

Glen Prior (geochemistry)
Alberta Geological Survey

4th Floor Twin Atria Building 4999 – 98 Ave,
Edmonton, Alberta Canada T6B 2X3
Email: roger.paulen@gov.ab.ca, john.pawlowicz@gov.ab.ca, glen.prior@gov.ab.ca

Coming soon in the AEG EXPLORE newsletter:

Technical articles and letters to the editor are encouraged as submissions for discussion within the newsletter. Each issue of EXPLORE contains a series of short discussion papers which provide either an update on a particular geochemical topic, or present current debates about issues of interest. Suggestions for future “Focus” topics may be forwarded to the editor, Mary Doherty (Email: MaryEDoherty@earthlink.net).

Issue: 119
Laboratory Update & Geochemical Standards
March 2003

Contributor Deadline February 28, 2003
Publication Date: April 2003

120 3-D Vectoring and Data Integration
Robert Jackson rgjackson@ctnis.com

Contributor Deadline May 31, 2003
Publication Date: July 2003

121 Environmental Geochemistry Update
Rob Bowell rbowell@srk.co.uk/srk003@aol.com

Contributor Deadline August 31, 2003
Publication Date: October 2003

122 Soil Gas Chemistry
Patrick Highsmith phighsmith@aschemex.com

Contributor Deadline November 30, 2003
Publication Date: January 2004
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12. A member shall not use, whether directly or indirectly, any confidential information of an employer or client which is in any way competitive, adverse, or detrimental to the interest of such employer or client.

13. A member restrained by one client shall not accept, without that client’s written consent, an engagement by another client if the interests of the two clients in any way conflict.

14. A member who has obtained by secret information during the course of this work for any employer or client shall not seek to make a personal profit from such information unless permission in writing to do so is granted by such employer or client, or until it is clear that the use of such information by the member shall not prejudice the employer or client in any way.

15. A member shall not divulge information given to him in confidence.

16. A member shall engage, or advise his employer or client to engage, and cooperate with other experts and specialists whenever the employer’s or client’s interests would be best served by engaging and cooperating with such experts and specialists.

17. A member shall not accept a concealed fee or secret commission for referring a client or employer to a specialist or for recommending geochemical services other than his own.

GEOANALYSIS
5th International Conference on the Analysis of Geological & Environmental Materials
8th–11th June 2003
Arktikum Building
Rovaniemi, Finland
Organised by Geological Survey of Finland
www.gsf.fi/geoanalysis/geoanalysis2003

GTK
and International Association of Geoanalysts
www.geoanalyst.org

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DUTIES OF MEMBERS TO EACH OTHER

18. A member shall not falsely or maliciously attempt to injure the reputation or business of another member.

19. A member shall not state as his own knowledge or belief information which he has obtained from another member and shall freely attribute other members as the source of such knowledge or belief.

20. A member shall endeavor to cooperate with other exploration geochemists in the study and dissemination of exploration geochemistry.

DUTIES OF MEMBERS TO THE ASSOCIATION

21. A member shall endeavor to ensure that candidates for membership are fit and proper persons to be elected members.

22. It shall be the duty of every member not only to uphold the standards of this Code of Ethics in precept and by example, but also, where necessary, to encourage by counsel and advice to other members, their adherence to such standards.

**Prospectors and Developers Association of Canada (PDAC)**

**Short Course 2: Indicator mineral methods in mineral exploration**

Saturday, March 8, 2003 (9:00 am-5:00pm) • Registration desk opens at 8:00 am

**Organizers:** Harvey Thorleifson and Beth McClenaghan, Geological Survey of Canada, Ottawa

Kimberlite indicator mineral tracing and an expanding number of other indicator mineral methods are becoming increasingly effective. This one-day workshop will review principles, methods, and developments in indicator mineral methods, which rely on sampling of sediments such as glacial and stream sediments, and detection of mineral deposit indicators dispersed by mechanical processes. The course will describe how indicator mineral methods are part of a spectrum of clastic sediment-based methods ranging from boulder tracing to detection of detrital debris or their weathering products by chemical analysis of C-horizon soils and sediments. The scope of these methods is expanding from the search for kimberlite indicator minerals to base metals and associated alteration.

**Topics to be addressed:**

- Indicator mineral survey design
- Sampling, processing and quality assurance
- Indicator mineral grain morphology
- Mineral chemistry
- Interpretation and follow-up


**Course fee:** Course fee includes course material, lunch and refreshments. Registration will be available after December 2, 2002. For payment received by February 1, 2003: $325 Can. For payment received after February 1, 2003: $525 Can.

**For more information:**

PDAC, 34 King Street East, Suite 900 Toronto, Ontario M5C 2X8 CANADA

Tel: (416) 362 1969 Fax: (416) 362 0101 Email: info@pdac.ca Website: www.pdac.ca.
Association of Exploration Geochemists
APPLICATION FOR MEMBERSHIP*

Please complete only the relevant section for membership. See below for mailing instructions.

I, ________________________________________________________________________, wish to apply for election as a __Member / __Student Member of the Association of Exploration Geochemists. I have read the Code of Ethics of the Association and in the event of being elected a Member/Student Member agree to honour and abide by them.

MEMBER: State Employer and Employee title
I am actively engaged in scientific or technological work related to geochemical exploration and have been so for the past two years.

(employer) (employment title)

STUDENT MEMBER: Student status must be verified by a Professor of your institution or a Fellow of the AEG
I certify that the applicant is a full-time student at _____________________________________________________________________________ in pure or applied science.

(institution)

(Professor/AEG Fellow Signature) (Printed Name and Title)

Witness my hand this _____ day of __________ , 20____

(Signature of applicant)

NAME AND ADDRESS: PLEASE PRINT (to be completed by applicant)

Name: ____________________________________________________________________________

Address: ____________________________________________________________________________

Telephone bus: ______________________________________________________________________

Fax: _______________________________________________________________________________

Home: ______________________________________________________________________________

e-mail: ___________________________________________________________________________

Annual Dues:

All applications must be accompanied by annual dues. All payments must be in US funds. Select one of the four listed below.

1 2003 member dues US$ 70 __________
2 2003 student member dues 40 __________
- If receipt required, include a self-addressed envelope and add
  2 __________
- If your check is not drawn from a U.S.A. or Canadian bank, add
  15 __________

TOTAL __________

Payment by check, International Money Order, UNESCO Coupons, International Postal Orders, VISA, American Express and Master Card are acceptable. For credit cards users, minor variations in your billing may reflect currency exchange rate fluctuations at time of bank transaction.

Type: VISA __ American Express __ Master Card __ Credit card account number: ________________________________

Expiry date: __________ Name: ________________________________

Signature: ________________________________

*Application for voting membership requires the sponsorship of three voting members. Request a voting member application from the Association office.

Please note: Your application form will be acknowledged upon receipt. The Admissions Committee reviews all applications and submits recommendations to Council, who will review these recommendations at the next Council Meeting or by correspondence. If no objection is raised the names, addresses and positions of candidates will be listed in the next issue of the AEG Newsletter. If after a minimum of 60 days have elapsed following submission of candidate information to the membership no signed letters objecting to candidates admission are received by the Secretary of the Association from any Member, the Candidate shall be deemed elected, subject to the receipt by the Association of payment of required dues. Send completed application, together with annual dues to:

Association of Exploration Geochemists
P.O. Box 26099, 72 Robertson Road, Ottawa, Ontario, CANADA K2H 9R0
TEL: (613) 828-0199, FAX: (613) 828-9288, email: aeg@synapse.net WEBSITE: http://www.aeg.org
RECENT PAPERS

This list comprises titles that have appeared in major publications since the compilation in EXPLORi Number 117. Journals routinely covered and abbreviations used are as follows: Economic Geology (EG); Geochemical et Cosmochimica Acta (GCA); the USGS Circular (USGS Cir); and Open File Report (USGS OFR); Geological Survey of Canada papers (GSC paper) and Open File Report (GSC OFR); Bulletin of the Canadian Institute of Mining and Metallurgy (CIM Bull.); Transactions of Institute of Mining and Metallurgy, Section B: Applied Earth Sciences (Trans. 1MM). Publications less frequently cited are included in full.


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RECENT PAPERS
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Please send additional references for citation to:

L. Graham Closs, Chairman AEG Bibliography Committee
Department of Geology and Geological Engineering
Colorado School of Mines, Golden, CO 80401-1887 USA
Email: lcloss@mines.edu

Association of Exploration Geochemists
SHORT COURSES

Periodically, the AEG sponsors short courses that can be presented at conferences or to any interested groups. Typically, the proceeds from registration would be applied to the costs of the presenter(s). If you are interested in having a course presented on any of the following topics, please contact Colin Dunn at the address below in order to discuss details.

Courses Currently Available for Presentation

- ‘Lithogeochemistry: Pearce Element Ratio Analysis’ - Cliff Stanley
- ‘Introduction to exploration geochemistry – including basic statistics, analysis and drainage sediments’ – K. Fletcher
- ‘Organic media in mineral exploration and environmental studies’, and variations on that theme, such as ‘Applied Biogeochemical Prospecting’ – Colin Dunn. These courses can include detailed modules by Gwendy Hall (for the analytical component), and Rob Scagel (for the forestry/botanical component).
- NEW - ‘Hyperspectral Imagery Applied to Mineral Exploration’ - Sandra L. Perry
- NEW - ‘Introduction to Hydrogeochemistry’ - Patrice de Caritat, David Gray, Dirk Kirste and Bear McPhail.

Colin E. Dunn, AEG Short Course Committee Co-chair, Sidney, BC, Canada
Telephone: 1-250-655-9498, Email: colindunn@shaw.ca
Readers’ Forum

**Membership Discussion: AEG name change**

Fellows of the AEG have recently voted on two proposals: 1) a change in the Preamble to the By-Laws, and 2) a change in the name of the Association itself. The change in the Preamble was deemed to be necessary to broaden the scope of the AEG by eliminating artificial barriers between exploration and environmental geochemistry. These revisions to the Preamble received strong support and will be incorporated in the broader revision of the By-Laws which will be circulated in 2003.

The vote on the change in the name of the Association produced a much less clear-cut result. Why was this? A name change is a major step in any organisation and must be thought through with great care. The main issues need to be identified, and we believe that perhaps this was not done sufficiently in the lead-up to the vote on the name change. In an effort to bring the debate more into focus we would like to suggest that there are just two major requirements for a new name. It should be: 1. Discipline-neutral (otherwise we could be trying to change the name again in the not too distant future), and 2. Marketable.

Judged against these criteria, one proposed name – *Association of Exploration and Environmental Geochemists* – would seem to fail on both counts. It is very specific and exclusive but at the same time is sufficiently cumbersome that it would pose major marketing challenges. Given our decline in membership in recent years, marketing to potential new members will be absolutely critical. We believe that the alternative proposal – *Association of Applied Geochemists* – measures up much better against the two major requirements.

We are faced with an extremely important decision on the name change of the Association, a decision that has the potential to affect us for many years to come. We urge all members to become involved in this debate either through the Members’ section of the web-site, through the pages of EXPLOR or by direct correspondence.

David Garnett, Gerry Govett, **AUSTRALIA**
Bob Garrett, Gwendy Hall, Ian Nichol, Ashlyn Armour-Brown, Barry Smeel, **CANADA**
Xueqiu Wang, **CHINA**
Alecos Demetriades, **GREECE**
L. Graham Closs, Lloyd James, David Kelley **USA**

I am not in favour of the name change to Association of Exploration and Environmental Geochemists. The word “exploration” can be interpreted as “mineral exploration”, “environmental exploration” and so on. Thus, “exploration” is a research methodology, but “environment” is a research
Reader's Forum...

objective. These two words are incompatible to modify "geochemists". I do hope we deliberately consider the change of AEG name. I think the best choice is that we do not change the AEG name until we find an appropriate name.

It can be acceptable the change of the Association of Applied Geochemists if we do want to change the name.

All the members in China strongly object to replace the name of “exploration geochemistry” with “geochemistry of mineral resources” in the Preamble to the AEG By-Laws. It can be acceptable if we change Exploration Geochemistry to Geochemistry of Natural Resources. Mineral, oil, forest, ocean, and land resources should definitely be included in the AEG field. In China, exploration geochemical data have already been used in land monitoring, agricultural production increase, ocean resource surveying and so on. In addition, the “exploration geochemistry” has broader and wider meanings than “geochemistry of mineral resources.” The word of “exploration” can be interpreted as “mineral exploration,” “environmental exploration” and so on.

Xueqiu Wang, China
xqwang@heinfo.net

The Association of Exploration Geochemists Journal

GEOCHEMISTRY:
Exploration, Environment, Analysis

Editor-in-Chief
G.E.M. Hall (Canada) e-mail: GHall@NRCan.gc.ca
Associate Editors
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The GEEA Journal covers all aspects of the application of geochemistry to the exploration and study of mineral resources, and related fields, including the geochemistry of the environment. Topics include: the description and evaluation of new and improved methods of geochemical exploration; sampling and analytical techniques and methods of interpretation; geochemical distributions in and around mineralized environments; and processes of geochemical dispersion in rocks, soils, vegetation, water and the atmosphere. Papers that seek to integrate geological, geochemical and geophysical methods of exploration are particularly welcome. Given the many links between exploration and environmental geochemistry, the journal encourages the exchange of concepts and data; in particular, to develop mineral resources while protecting the environment. Submission of Letters to the Editor is encouraged; this provides a means of commenting on papers that have been published in the journal. GEEA is published by the Geological Society of London.
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WHEN YOU NEED TO BE SURE

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Newsletter for The Association of Exploration Geochemists
P.O. Box 150991, Lakewood, CO, 80215-0991, USA

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P.O. Box 26099, 72 Robertson Road, Nepean, Ontario, K2H 9R0, Canada • TEL: (613) 828-0199 FAX: (613) 828-9288
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