



Special thanks to Patrick Highsmith for assembling
focus topics for this issue,
Soil Gas Chemistry

Overview of Soil Gas Theory

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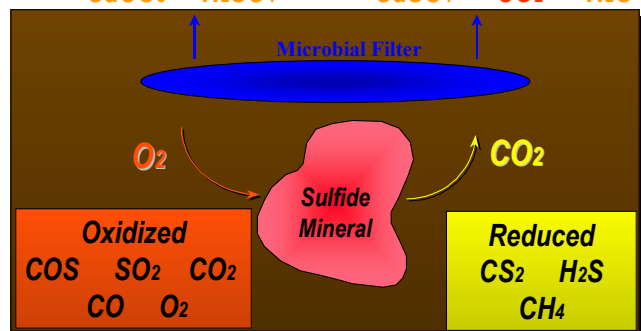
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Mineral exploration is being irreversibly forced into covered terranes. After all, we have been hearing for several years that “all the easy ones have been found”. While this is arguably a platitude, or even an excuse for some, it is largely true. At the very least, we are all working in more mature areas, often where the prospective rocks are not exposed. As commodity prices surge, hopefully dragging exploration budgets along for the ride, exploration is returning to areas of deep overburden and explorers seem more willing to invest in new technologies to probe these depths.

Soil gases remain a tantalizing sample medium for mineral exploration in covered terrane - at least for some of us. Dating back to the mid-1950's in the Soviet Union, explorers have considered the gaseous products of sulfide oxidation as a target sample medium. Western geologists and geochemists made serious forays into soil gas geochemistry for mineral exploration as evidenced by three important PhD dissertations on the subject (Lovell, 1979; Oakes, 1984; and Jaacks, 1984). During the 1980's, significant advances in the practical application of the technology followed, but much of this was veiled in company secrecy. Klusman (1993) authored the definitive text on the subject, incorporating summaries of past work and numerous case studies from different sample media in many applications.

Soil Gas Geochemistry Operating Principle



Modified after Jaacks, 1993

Figure 1 - Simplified Model for Soil Gas Genesis

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At its most basic level, soil gas geochemistry is attractive for exploring beneath overburden because of the very high mobility of gases. It is easy to imagine gases moving rapidly upward through overburden. If the gases reaching the surface includes a signature of buried mineral deposits, their utility as a prospecting tool is obvious.

The concept of gas generation and migration is actually a complex interplay among many elements, gaseous compounds, and environmental variables. Consider a long list of gases that may be involved and have been addressed, at least superficially in the literature:

- Simple, abundant, inorganic gases (O_2 , CO_2 , N_2)
- Sulfur gases related to sulfide mineralization (H_2S , COS , CS_2 , etc.)
- Volatile metals and semi-metallic hydrides (AsH_3 , SbH_3 , Hg , etc.)
- Light and heavy hydrocarbons ($C_2 - C_{17}$)
- Radiogenic daughter gases (He , Rn)

The Model and Processes at Work

Figure 1 (see front page) is a simplified model illustrating the involvement of oxygen and carbon dioxide in the oxidation of sulfide minerals. A simple sulfide mineral, pyrite, is shown to be oxidizing in the presence of water. Through a series of reactions, oxygen is consumed and iron oxide and acidity are the reaction products. The resulting acid reacts with any available carbonate in the wallrocks generating carbon dioxide. Taylor et al (1982) demonstrated experimentally that a number of the sulfur gases cited on the diagram are generated during this oxidation process. Attempting to incorporate the microbiological variable in these reactions, the blue oval is meant to suggest a degree of catalysis or facilitation by microorganisms, which is likely not yet fully understood.

Many of the soil gas references in the literature cite some variant of this primary oxidation process as the most likely source of the gaseous target agents. There are a few problems with this process being accountable for gases that are measured at the surface. Not the least of these problems is the water table. If the mineral deposit is below the water table, as it is in a number of the case studies cited below, there may not be adequate available oxygen to drive sulfide oxidation. Even if there is adequate oxygen, many of these compounds would be dissolved into the groundwater, having insufficient vapor pressure to elute as bubbles and rise by buoyancy through the water table.

Furthermore, many of the gases listed above are reduced compounds, highly unstable in the presence of oxygen (H_2S , heavy hydrocarbons, and the hydrides). This means that they would not survive long enough to reach the surface, even if generated at a point of oxidation well above the water table (Taylor et al, 1982).

The glass is half full however; soil gas enthusiasts fear not! Recent overburden geochemistry research has significantly improved our understanding of at least one process that may be responsible for moving trace elements and gases through overburden. As part of CAMIRO and

Ontario Geological Survey/Geological Survey of Canada research projects on overburden geochemistry in Canada, Stewart Hamilton and co-authors are developing an improved model to account for transport of trace elements through overburden (Figure 2). The investigators have demonstrated the presence of a reduced column above mineral deposits in the Abitibi clay belt of northeastern Ontario. This gradient in oxidation potential is postulated to be the driving mechanism for redistributing elements in the overburden, possibly explaining anomalies in partial leaches and other geochemical techniques. (Hamilton, 2000; Hamilton et al, 2004A, and Hamilton et al, 2004B)

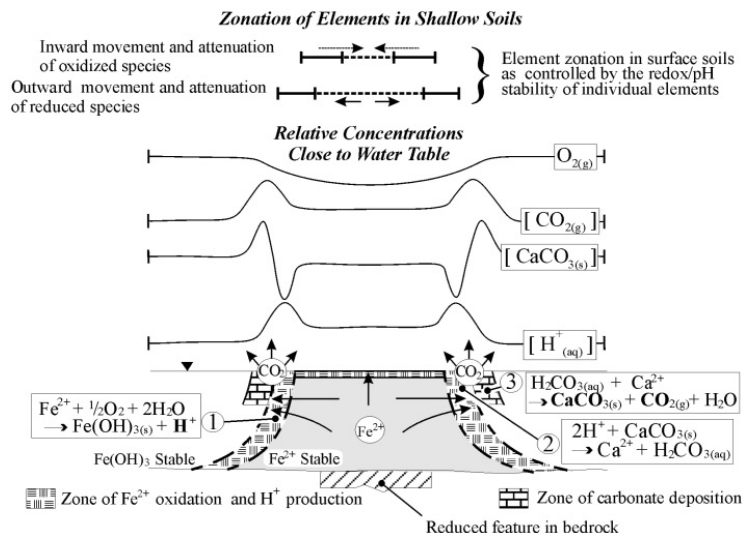


Figure 2 - Model for Development of Geochemical Anomalies by Electrochemical Processes. Hamilton et al, 2004A.

While not yet specifically addressing the migration or fixation of soil gases at the surface, the implications of this process are important to soil gas dispersion theory. The presence of a reduced column in the overburden above a mineral deposit should cultivate the propagation of reduced gaseous species. Inasmuch as the presence of a “reduced column” is a matter of relative abundance of reduced versus oxidized species, this phenomenon almost certainly extends above the water table to some degree. Gaseous migration above the water table may therefore be influenced by this reducing environment. However, the infinite oxidizing capacity of the atmosphere dramatically threatens the stability of reduced gases near the atmospheric interface.

Nonetheless, anomalous concentrations of reduced gases, derived from numerous sample media, are reported in this issue and in the literature. Surely there is something to these reports. Perhaps we need to consider other mechanisms for the genesis of these gaseous species. While some isotopic evidence exists, as yet there is insufficient research to categorically link any gaseous signature at the surface to a subsurface source. In certain environments the oxidation-reduction model does constitute a viable mechanism for some gaseous anomalies.

The flanks and top of the reduced column are, by definition, undergoing active oxidation. As shown in Figure 2, this zone can be a major oxygen consumer. The acid attack

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on any local carbonates could also result in significant carbon dioxide off-gassing. That reduction/oxidation (Redox) interface could also result in the liberation of certain sulfur gases. Viewed in this context, this oxidation potential model merely translates the site of active oxidation upwards to the top of the reduced column, which is more realistic when the mineral deposit is far below the water table.

Importantly, major redox boundaries are very often heavily colonized by bacteria. Such microbial population centers are likely sources of gases resulting from their metabolic processes (e.g., CO_2 , CH_4 , H_2S). (Ehrlich, 1996.) Furthermore, the sheer biomass along these redox interfaces may be a significant source of organic carbon, subject to volatilization as hydrocarbons. If a surface soil sample is anomalously rich in certain types of microbial life, perhaps it could produce an organic gas response when thermally treated or ionized. If this were true, the “soil gases” released during desorption would actually be an indication of anomalous biota rather than direct gas flux. Research is currently underway in Canada to better understand the occurrence of bacteria in soils over mineral deposits, particularly associated with local pH and oxidation-reduction potential (ORP) anomalies.

The point of interest here is that some of the soil gas we measure over mineral deposits could be an indirect response caused by processes such as microbial metabolism and oxidation of reduced species some distance above the mineral deposit. As empirical explorers, we are interested in reproducible patterns that are indicative of mineralization, whether or not we fully understand the mechanism. Therefore, using soil gas geochemistry, we hope to uncover evidence of these processes in whole gas samples from soil pore spaces or as gaseous species sorbed to adsorbent substrate in the near surface.

According to this redox model and its logical extensions, there may be considerable crossover between low concentration soil geochemical methods, such as partial leaches, and soil gas geochemistry. This is particularly true today because most commercially available “soil gas” techniques are based on soil desorption principles. Are the gases, in fact, indicators of the redox processes, just as some of the elements detected in partial leaches are redox active?

Powerful processes are no doubt at work here. It is tempting to try to describe them in terms of a continuum, extending from basic physio-chemical concepts, that account for geochemical responses in soil and soil gas. Figure 3, a hypothetical and idealized cross section view, theorizes a complex structural “plumbing system” superimposed on Hamilton’s redox model. A hypothetical geochemical profile reflects the sort of patterns which are commonly seen in soil and soil gas geochemical analyses. The oxidation-reduction gradient re-mobilizes many constituents of the mineral deposit environment, and at the water table some volatile participation is highly likely (CO_2 , O_2 , sulfur gases, and light hydrocarbons). Given the proposed strong structural control on geochemical patterns, various theories for migration of trace elements, such as evapotranspiration and seismic

pumping, could also be accommodated in this model.

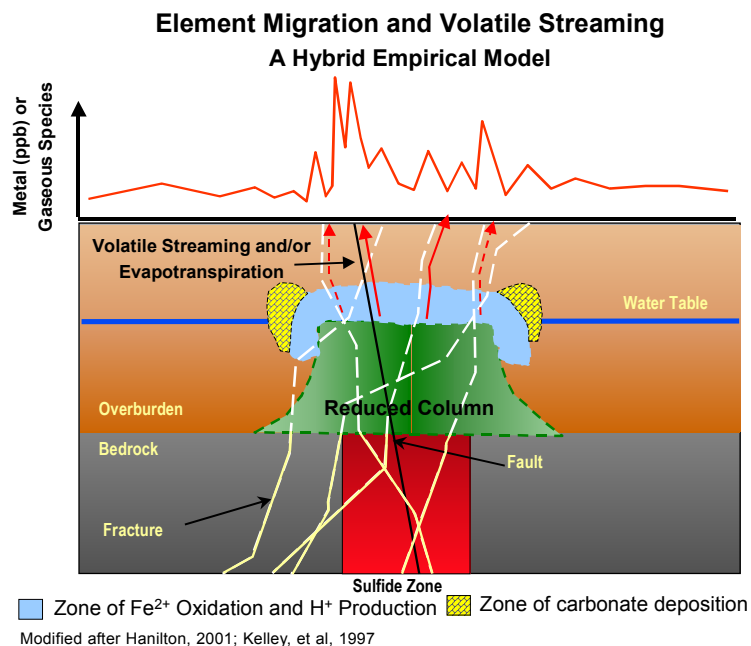


Figure 3 - Proposed Model for RedOx Driven Volatile Streaming and Element Migration

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Introduction to Soil Gas Methodologies

While some of the theory behind soil gas geochemistry is undefined, we haven't let that stand in the way of getting out and sniffing gas! There are several options available for adding this tool to your exploration programs. Four different soil gas methodologies are described below. Three of these four are provided as a commercial analysis on soil samples. The fourth technique is based on sampling whole soil gases with a probe based system measuring CO₂ and O₂.

The following reviews of soil gas techniques are presented by the service providers or developers of the methods. Soil gas methods fall into two categories: whole gas methods and desorption based methods. Herein we have contributions determining instantaneous CO₂ and O₂, and three commercial adsorption based techniques:

- Gas'm Mercury Analysis
- Soil Desorption Pyrolysis (SDP)
- Soil Gas Hydrocarbons (SGH)

Desorption Based Soil Gas Methods

The concept behind soil gas collectors is that the gas signal is sampled over time, thus integrating the response. The integrated sampling should be less susceptible to meteorological changes and other sources of short-term variance. Desorption of soil gases also has the added benefit of being practicable where extraction of pore space gases is not possible, such as saturated ground or very shallow water tables. Adsorption based soil gas methods come in two basic

forms: static trapping devices or natural collectors. The three methods discussed here all rely on some fraction of soil samples to collect a mobile gas phase. Once collected, the gaseous target compounds may be extracted by solvent digestion or some sort of thermal desorption. A myriad of gaseous targets are available, but some providers focus on narrower families of gases.

There are a few techniques for sampling soil gases using engineered collectors, such as activated charcoal, the Gore Sorber® module, or the BRGM soil gas cups. These collectors are generally deployed for a period of weeks prior to collection and analysis. These types of static trapping devices have never been very popular in mineral exploration, partly because of their perceived complexity and cost and partly because multiple trips to the field are required. However, an engineered sorption substrate has certain advantages with respect to sampling specificity, desorption characteristics, and possibly sensitivity. An engineered sorbant should also be more homogeneous than natural sample media, thus precision may be improved.

There is a considerable volume of work with soil gas collectors methods in the petroleum field. Microseepage of hydrocarbons to the surface is documented over petroleum reservoirs (Klusman, 1993). Of course, there is an important distinction to be made here between the high vapor pressures of light hydrocarbons in petroleum reservoirs and the trace hydrocarbon gases likely to evolve from mineral deposits.

Natural media, such as soils, require only one field visit and have been "deployed" through geologic time. Therefore the soil gas signal should be less susceptible to sampling error and theoretically more robust and precise than short term sampling. Any natural sample medium will be

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inhomogeneous however, so the desorption characteristics may vary from sample to sample. Since the specifics of desorption or extraction conditions may not be known, there may also be questions about the source of the desorbed gases.

In recent years, considerable development has taken place in working with soil desorption and volatiles analysis. One advantage of this approach is that the samples are returned to a lab for analysis, where state-of-the-art analytical technology can be brought to bear. The commercial methods reported herein rely on sophisticated analytical technology to achieve sub-ppb detection limits for many gases. While admirable strides have been made, the per sample costs still reflect the laboratory infrastructure required.

Whole Gas Soil Gas Methods

Whole gas methods rely on extraction of the gases from the soil pore spaces using probes and some sort of pumping system. The gas can be collected for later analysis or analyzed immediately in the field. Various techniques have been used over the years, but the most popular derivations are multi-gas analysis by mass spectrometer and carbon dioxide/oxygen analyses with portable analyzers.

Howard McCarthy of the USGS has worked extensively on the measurement of soil gases in various terranes with a vehicle mounted mass spectrometer (McCarthy et al, 1986A & B). Whereas, Lovell (1979) and Lovell et al (1979, 1980, and 1983) reported on the forerunner of the current carbon dioxide/oxygen sampling system developed and modified by Jaacks (pers. comm.) and this author. The fundamental differences between McCarthy's multi-gas work and the CO₂/O₂ work reported below are the complexity of the analytical finish, the sample volumes, and the portability of the field equipment. Carbon dioxide and oxygen are stable gases occurring in percentage levels that are easily measured in the field. As discussed above, these two gases are useful indicators of mineral deposits because of their participation in oxidation-reduction (RedOx) related processes. However, the low cost is one of the driving factors behind the development of the carbon dioxide-oxygen method.

Real time extraction of soil gases is subject to a number of complexities, principle among them are meteorological variation and variable biological activity (Klusman, 1993). However, careful field craft can moderate most of these effects. The carbon dioxide and oxygen method discussed herein always includes base stations in order to monitor changing meteorological effects and background fluctuations.

The State of Commercial Applications

Consider the four methods discussed elsewhere in this issue. As noted above, much of the development of soil gas technologies has been empirically based. These brief overviews do not offer enough space to explain any of the methods in detail.

Some of the contributions assume some knowledge of the methods, while others have provided more background

information. Hopefully this introductory section will assist the reader with theoretical background and some history on the philosophy of soil gas practitioners. Interested parties are encouraged to review some of the references provided and to contact the providers of these services directly.

There are marked differences among the methods. In general, the offerings discussed here range from the "do-it-yourself" and less expensive single or double analyte methods (Gas'm mercury and CO₂/O₂) to the more expensive and complex multi-gas data reported from mass spectrometers or gas chromatograph-mass spectrometers (SDP and SGH).

The different philosophies among the service providers and technical practitioners are apparent in the details, or lack thereof. It is apparent that some of the discussions of the proprietary methods withhold considerable detail. There is also much emphasis on sophisticated data processing from the purveyors of SDP and SGH. The mercury and oxygen-carbon dioxide methods rely much more on pattern recognition; no recipe is offered for target fingerprinting. These realities place a considerable burden on the geochemist in selecting methods. Either the client must place a huge amount of trust in the service provider or there is an inescapable need for orientation surveys to provide the confidence for large-scale application. As discussed above, the exact genesis of the touted gaseous responses is not well understood, nor are there convincing examples of "soil gas discoveries" described in this issue or the literature.

Perhaps it is not difficult to understand why soil gas geochemistry has seen such limited wide-scale application. Exploration technologists should be empiricists, so there's no requirement for every question to be answered. However, discoveries are hard to come by; and they usually originate from multi-discipline data. In the absence of spectacular documented success, it is wise to seek a reasonable theoretical understanding of our exploration tools. The reader is encouraged to consider the scientific theory behind soil gas geochemistry, review some of the fundamental references provided herein, and evaluate the various methods in that context. Only then will the service providers and experienced consultants be pressed to improve the fundamentals and make the breakthroughs which will lead to discovery.

While it is exciting to see such an unprecedented variety of soil gas services available to the mineral explorer, it remains to be seen whether any method will gain wide acceptance with so many unanswered questions. Meanwhile, a few intrepid exploration groups are applying systematic soil gas geochemistry on their projects. It promises to be very interesting as their results become known. A few confirmed discoveries would fuel the fire like no technical diatribe ever could!

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