Mineral deposits and chalcogen gases

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Abstract

Sulphide minerals and their analogues yield gases as a result of oxidation reactions. Even where sulphide minerals are in contact with mildly reducing groundwaters, S^{2-} ions pass into solution and their dispersion patterns can be detected in soil as acid-released H_2S. In more oxidising conditions, the metastable gases COS and CS_2 are generated. Anomalous dispersion patterns of COS have been reported in soils above more than ten sulphide ore deposits, many of them concealed beneath transported exotic overburden. High concentrations of CS_2 occur in the soils over several of the same deposits and uniquely reflect others. Anomalies of SO_2 over sulphide deposits are confined to arid terrains. Certain anomalous dispersion patterns of arsenic and tellurium in soils are attributed to the generation and migration of unspecified gases from the oxidation of arsenide and telluride minerals.

KEYWORDS: chalcogen gases, sulphide minerals, oxidation, arsenic, tellurium.

Introduction

THE resurrection of a term which fell into disuse well over a century ago creates the opportunity to offer a modern, geochemical definition. Here chalcogens are taken as those elements of Groups 5B and 6B of the Periodic Table that combine with metals in minerals which often constitute economic mineral deposits and which are unstable in the zone of oxidation (Fig. 1). It so happens that the breakdown products of these minerals include not only chalcogen-bearing secondary minerals, amorphous compounds and soluble anion complexes, but also chalcogen gases. By such a definition, polonium is not a chalcogen, but its chemical similarities and geochemical occurrence prompt its inclusion here.

The exceptionally small quantities of gases that are generated during mineral breakdown and the natural high mobility of gases tend to pose problems for their detection. A characteristic of the chalcogens, however, is that their gas phase dispersion is partially constrained by gas adsorption onto active surfaces within soils. This retention results in an accumulation of these gases on soils, which also constitute a convenient medium for collection and transportation of the gases to the analytical laboratory.

Dispersion patterns of chalcogen gases in soils can therefore be used to obtain a geochemical expression of the occurrence of their parent minerals. This assumes particular importance in exploration situations where conventional geo-

INERT GASES					
3B	4B	5B	6B	7B	2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 (At)	86 Rn

FIG. 1. Position of the chalcogens (shaded) and polonium in the Periodic Table.

chemistry fails, for example, where blind mineralization is sought beneath unmineralized bedrock

or concealed mineralisation is sought in bedrock beneath transported exotic overburden.

Sulphur gases and other Group 6B chalcogens

Many metals are found as economic deposits in the form of sulphide minerals. During the oxidation of these minerals, some of the their sulphur is transformed into gaseous compounds. The utility of any one of these sulphur gases for mineral exploration depends on the combination of a number of factors, including the propensity for its generation and its chemical properties, in particular, solubility in water and stability in air. Using equilibrium thermodynamics, Taylor et al. (1982) calculated that hydrogen sulphide (H_2S) should be the most abundant gas evolved by decomposing sulphides, followed by carbonyl sulphide (COS), carbon disulphide (CS_2), methyl mercaptan (CH_3SH) and sulphur dioxiode (SO_2) (Fig. 2). In experiments which simulated weathering of pyrite and other common sulphides, Hinkle et al. (1990) found that the only sulphur gases liberated were CS_2, COS and SO_2, while Taylor et al. (1982) found only CS_2 and COS, in that order of abundance (Table 1). In fact COS and CS_2 are the least soluble of the sulphur gases, which may be a significant factor for their detection in the gas phase over mineral deposits experiencing oxidation under moist or saturated conditions. In addition COS and to a lesser extent CS_2 are the most stable in air, which favours their persistence during gas-phase dispersion through permeable rocks and overburden. The greater stability of COS is a particularly useful attribute for its survival during migration from deeply buried deposits to the near-surface environment. An important practical consideration is the way in which these gases occur in soil and overburden. Kesler and Gardner (1986) showed that in oxidation experiments in which pyrite was covered with sand, CS_2 tended to remain in the interstitial spaces whereas COS was adsorbed onto sand particle surfaces.

The geochemical analysis of soils for sulphur gases has usually been performed by equilibrating unsieved or sieved samples in gas-tight containers for several days at a constant temperature between 47 °C and 125 °C, and then loading an aliquot of the desorbed gases onto a suitable column in a gas chromatograph equipped with a flame photometric detector or a Hall electrolytic conductivity detector (Hinkle and Dilbert, 1984; Nicholson et al., 1988; Kesler et al., 1990). Using thermal desorption at 95 °C for one hour and the addition of hydrated silica gel to assist desorption from naturally dry samples, Oakes and Hale (1987) determined COS by gas chromatography with a column retention time of only 1.23 min (compared with around 8 min for the sequential determination of H_2S, COS, SO_2 and CS_2) and a limit of detection of about 2 pg COS per 1 g of soil. Jin et al. (1989) determined H_2S at sample sites by injecting HCl into a sealed hole in the soil and releasing S^{2-} adsorbed on the soil as H_2S gas, which was passed to a lead acetate detector by pumping the air from the hole for 1 min.

Hydrogen sulphide. After confirming that only extremely low levels of H_2S occur in the pore spaces of soils above mineral deposits, over 20 surveys were carried out at porphyry copper, porphyritic iron, altered-breccia gold and volcanic breccia lead–zinc deposits in China in
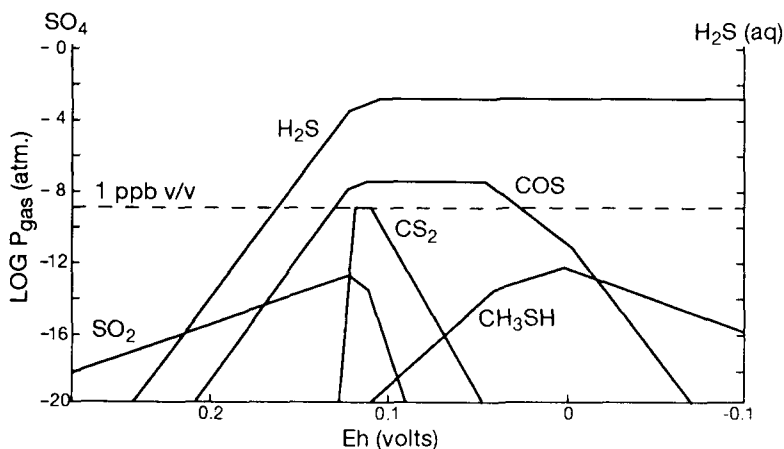

FIG. 2. Sulphur gases in equilibrium with aqueous sulphur species at pH 2.5 (from Oakes and Hale, 1987).

Table 1. Generation of sulphur gases through sulphide decomposition and their solubility in water and stability in air

Gas	Ranked abundance during sulphide decomposition *		Solubility in water @ 20°C (g/100 ml)	Stability in air (days)
	Calculated	Experimental		
H_2S	1	nd	0.44	1
COS	2	2	0.20	600
CS_2	3	1	0.22	40
CH_3SH	4	nd	-	-
$(CH_3)_2S$	5	nd	-	3
SO_2	5	nd	17.2	9

* From Taylor et al. (1982)

which S^{2-}, dispersed in groundwater following natural sulphide oxidation and subsequently adsorbed onto soils, was converted into H_2S for determination as described above. Only four surveys failed to reveal acid-released H_2S anomalies. Jin et al. (op. cit.) summarise the results from a survey over a cupriferous pyrite skarn at Baijiacun, Shanghai, which plunges westward along the contact zone between granodiorite and interlayered marbles in hornfels, and is concealed beneath 140 to 160 m of transported Quaternary sediments, on which a thick soil cover has developed. Four traverses, 100 to 200 m apart, were sampled at intervals of 20 m; the three traverses in the east of the area crossed mineralisation known at the time of sampling, while the most westerly traverse was in an unexplored area. High-contrast H_2S anomalies occur over the mineralisation on the most easterly traverse (Fig. 3). Further west over the mineralised contact zone, progressively weaker anomalies are present, reflecting the downplunge continuation of the mineralisation. On the most westerly traverse, another high contrast H_2S anomaly was found to the north of the known mineralised contact zone; a year after the H_2S survey a second cupriferous pyrite orebody was discovered beneath this anomaly.

Carbonyl sulphide. Low concentrations of COS (and H_2S) over mineralisation were first reported by Hinkle and Kantor (1978), who absorbed gases on molecular sieves left in inverted glass jars 30–45 cm below the surface for eight weeks. Accumulation of COS by natural soils was demonstrated by Lovell et al. (1980). At the Yankee prospect, a sediment-hosted micron gold deposit near to Alligator Ridge, Nevada, Kesler et al (1990) determined COS and other gases in unsieved soils, sieved soils, gas absorbers and soil air. The best results were obtained with gases thermally desorbed from unsieved soils, and elevated COS values were found over mineralisation and faults.

Oakes (1984) showed that the <150 μm fraction soils was, in many cases, relatively enriched in COS, and Oakes and Hale (1987) determined the COS content of this fraction of soils in surveys over a number of mineral deposits concealed
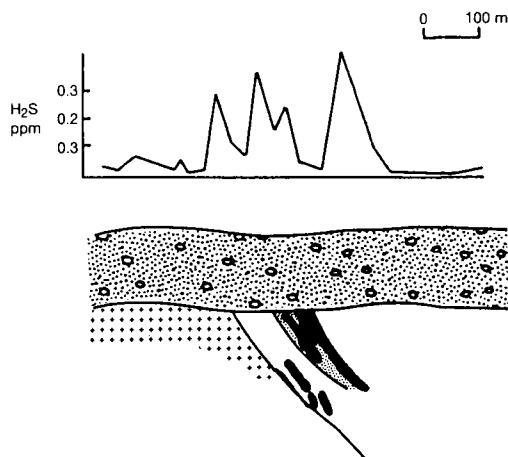

FIG. 3. Acid-released H_2S in soil air, Baijiacun, Shanghai: coarse stiple—Quaternary sediments; crosses—granodiorite; fine stiple—skarn; unshaded—hornfels; black—cupriferous pyrite (modified after Jin et al., 1989).

beneath different types of superficial cover: in arid and semi-arid regions with sparse vegetation the surface microlayer (the top few millimetres) of the overburden was sampled, sieved on site and stored in gas-tight containers prior to analysis; in temperate regions, the soil below the rooting depth of vegetation (typically 50 cm) was sampled using an auger and placed directly into gas-tight containers, from which it was removed, air dried and sieved immediately before analysis.

Near to Organ, New Mexico, chalcopyrite mineralisation grading up to 19% Cu occupies the Torpedo–Bennett fault zone, close to the contact between a quartz monzonite intrusive (which contains up to 10% pyrite) and recrystallised limestone; gossans outcrop in places but elsewhere mineralisation is concealed beneath 5–10 m of transported alluvial sands and pediment gravels.

In a traverse of surface microlayer samples, Oakes and Hale (1987) found that soils on unmineralised limestone contained less than 150 pg g^{-1} COS, those on quartz monzonite produced a COS background in the range 150–400 pg g^{-1} and the transported cover over the mineralised fault zone was characterised by a more erratic COS pattern, including anomalous peaks in the range 400–800 pg g^{-1} (Fig. 4).

At Johnson Camp, 110 km east of Tucson, Arizona, several gently dipping tabular replacement bodies of low-grade chalcopyrite–sphalerite occur in limestones, dolomites, shales and calcareous sands. The suboutcrops of the mineralised bodies are concealed beneath pediment gravels and alluvium, which increase in thickness from southwest to northeast and contain lenses of caliche. Oakes and Hale (1987) sampled the surface microlayer at intervals of 30 m along traverses 60 m apart, forming a grid 900 × 300 m, and found anomalies, exceeding 300 pg g^{-1} COS directly above the suboutcrop of mineralisation concealed beneath 90–150 m of transported overburden, compared with background levels around 100 pg g^{-1}. The anomalies are patchy, perhaps because of preferential gas migration in fractures in the host rock, displacement by runoff channels in the overburden or impeded gas migration due to layers of caliche.

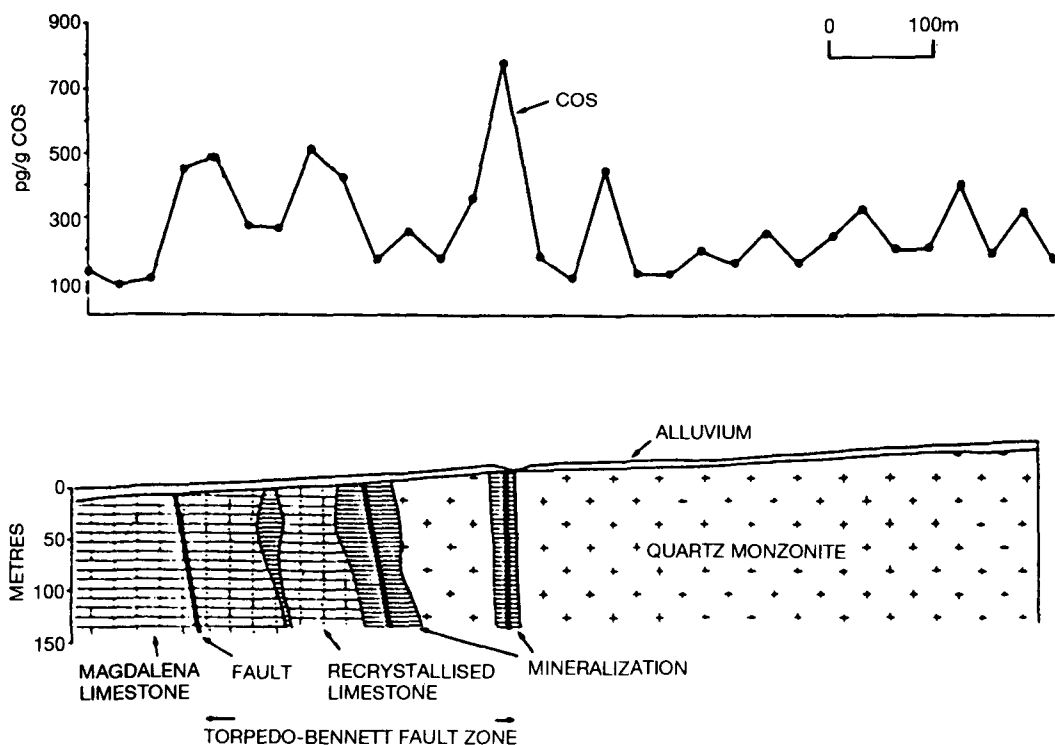Oakes and Hale (1987) also laid out a grid of surface microlayer samples over wadi sediments

Fig. 4. Simplified geology and COS in surface microlayer soils at Torpedo, New Mexico (reproduced with permission from Oakes and Hale, 1987).

at Ash Sha'ib, 500 km south of Jeddah, Saudi Arabia, where east–west striking stratabound zinc and copper sulphides intercalated with dolomitic marble and hornfels outcrop as a dark limonitic gossan and disappear westwards under wadi sediments. There are two subparallel anomalous zones of COS, with concentrations in excess of 400 pg g^{-1} and reaching 1500 pg g^{-1}, compared to a background of about 200 pg g^{-1}. The southern anomalous zone appears to follow the westward strike projection of the gossan outcrop, but information from subsequent trenching suggests that the anomalies coincide with palaeo channels in a wadi distributary system that probably drained the mineralisation at outcrop.

A traverse of surface microlayer samples from an undisclosed prospect, supplied to Oakes and Hale (1987) by an exploration organisation, initially yielded only three very weak COS anomalies. Re-analysed with hydrated silica gel to promote desorption, there were four anomalies in the range 300–400 pg g^{-1} COS compared to a background of 20–200 pg g^{-1} (Fig. 5). In both data sets, the anomalies occur over what was later revealed to be the gently-dipping sphalerite-rich polymetallic sulphide mineralisation at Geelvloer (northwest Cape Province, South Africa), which lies beneath about 10 m of mixed aeolian sand

and rock residue. The COS anomalies occur above the concealed suboutcrop of the mineralisation and its intersection with the water table.

Nicholson et al. (1988) determined COS and other sulphur gases in unsieved soils over six mineral deposits in the temperate regime of western Europe, and conclude that COS is present in the vicinity of only those deposits in which pyrite occurs as either massive pyritic sulphide or a gangue mineral within the ore. Oakes and Hale (1987) analysed samples from a depth of 50 cm in soils developed on the 2–7 m thick blanket of clay-rich Pleistocene glacial till that conceals the suboutcrop of sphalertie- and galena-mineralised faults and a metal-rich ferruginous horizon (the Decomposed Zone) at Keel, in the north-central part of Ireland. Background values are less than 400 pg g^{-1} COS, while peaks in excess of 750 pg g^{-1} reflect the main mineralised faults and the Decomposed Zone; values between 500–750 pg g^{-1} mark other mineralized and unmineralised faults.

Carbon disulphide and sulphur dioxide. Their investigations over mineral deposits in western Europe led Nicholson et al. (1988) to conclude that CS_2 soil anomalies accompany COS anomalies over mineral deposits with abundant pyrite, whilst only CS_2 is present where pyrite is an accessory mineral not directly associated with the
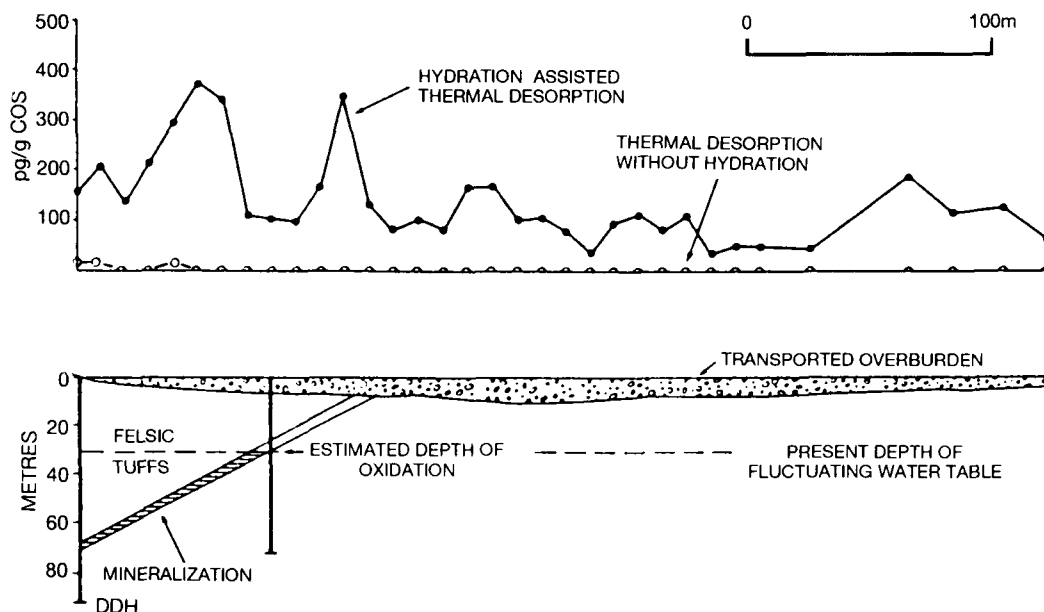

FIG. 5. Simplified geology and COS in surface microlayer soils at Geelvloer, South Africa (reproduced with permission from Oakes and Hale, 1987).

mineralisation. Hinkle and Dilbert (1984), using the <600 μm fraction of samples from the topmost 5 cm of residual soils over the North Silver Bell porphyry copper deposit in Arizona, found that CS_2 and SO_2 reflect the position of mineralisation better than COS (which reflects alteration zones around the orebody). The most abundant of these gases at North Silver Bell is CS_2, with concentrations in excess of 100 ppb over the orebody and roughly coincident with the highest concentrations of copper and molybdenum in soils (Fig. 6). The presence at North Silver Bell of anomalies of SO_2, which are more restricted in areal extent than those of CS_2 but reach peak values of more than 300 ppb over the orebody, are attributed to the shallowness of the ore deposit and the hot, dry environment. In the usually moist soils over mineral deposits in western Europe, Nicholson et al. (1988) found no SO_2.

Selenium and tellurium. Selenium is several orders of magnitude less abundant than sulphur (Table 2) and in soils it is intensively recycled by both oxidising and reducing biogenic reactions. Some of these generate gaseous dimethylselenide (Lakin, 1972), creating a high background which is not conducive to the detection of any gaseous selenium dispersion patterns derived from mineralisation. Although tellurium has a still lower natural abundance, Watterson et al. (1977) observed that tellurium soil anomalies are related to the intersections of the major structural elements in the Montezuma granodiorite porphyry, central Colorado, rather than to tellurium dispersion patterns in rock outcrops, and postulated that the soils may have accumulated tellurium from gaseous compounds emanating from mineralisation at depth.

Polonium. Uranium deposits at depth have been detected from dispersion halos of ^{222}Rn, a gas in the radiodecay chain of ^{238}U. This radon isotope subsequently decays via several very short-lived non-gaseous daughters to ^{210}Pb (half-life 22 years) and thence to ^{210}Po (half-life 138 days). Both ^{210}Pb and ^{210}Po are strongly adsorbed by soil and the collection of soil samples and the relatively easy laboratory determination of their ^{210}Po content therefore offer an alternative to the instrumental determination of ^{222}Rn at the field site or the emplacement and recovery of cups with alpha-particle detectors. An advantage of ^{210}Po is that its accumulation in the soil produces a long-timespan integrated signal, whereas the radon flux is variable. Dyck (1984) found a labile ^{210}Po anomaly in the C-horizon of soils over a radioactive boulder train at the Midwest uranium deposit, northern Saskatchewan; in the overlying horizons of the soil the anomaly is obscured as a result of the escape of ^{222}Rn to the atmosphere and precipitation of its daughter products back onto the surface soils. Card and Bell (1985) conclude that ^{210}Po anomalies in soil samples from a depth of only 25 cm at three uranium occurrences in Ontario are more clearly related to the presence of ^{226}Ra in the soil than to ^{222}Rn migration.
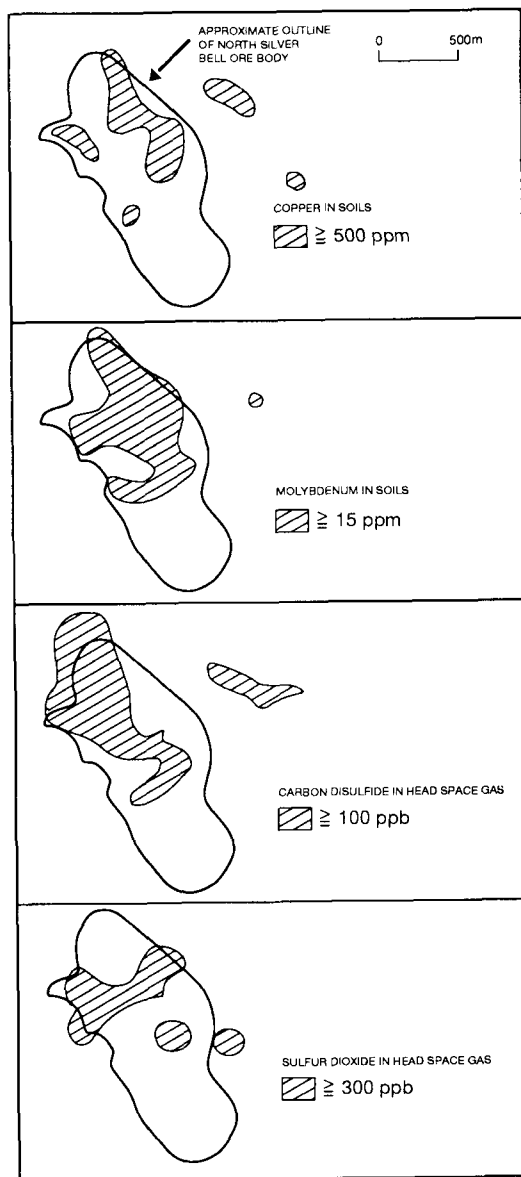

FIG. 6. Trace elements and desorbed gases in soils at North Silver Bell, Arizona (derived from Hinkle and Dilbert, 1984).

Table 2. Average abundance of chalcogens in the Earth's crust, various rocks and soil (ppm)

Element	Crust	Basalt	Granite	Soil
S	260	300	300	100 - 2000
As	1.8	2.0	1.5	1 - 50
Sb	0.2	0.2	0.2	5
Bi	0.17	0.15	0.1	0.8
Se	0.05	0.05	0.05	0.2
Te	0.001	0.001	0.001	0.01 - 0.001

From: Henderson (1982), Levinson (1980) and Rose et al. (1979).

Arsenic gases and other Group 5B chalcogens

Following the suggestion by Boyle and Jonasson (1973) that inorganic and organic arsenic compounds with relatively high volatility, such as arsine and dimethylarsine, are likely to occur in groundwater, spring water, bogs and soil air near to arseniferous mineral deposits, Ruan (1982) determined non-speciated arsenic in soil and soil air samples along a traverse crossing scheelite and arsenopyrite mineralisation in minor intrusive sheets of microgranite and quartz prophyry at Ballinglen, Ireland. Concentrations of volatile arsenic in soil air were determined by extracting 2 litre samples from a depth of 50 cm into absorption solutions (0.5% KI plus 0.1% I_2), which were then frozen to prevent loss of volatiles, and later defrosted in the laboratory immediately prior to analysis. Arsenic weakly adsorbed on soils was mechanically stripped from a slurry comprising 1 g soil in 5 ml deionised water by passing hydrogen gas at 500 ml min^{-1} for 3 min through the slurry to an absorption solution. The arsenic contents of both sets of absorption solutions were determined by adding a strong reducing agent to generate arsine and flushing this into an inductively coupled plasma emission spectrometer. Anomalies of volatile arsenic in soil air occur close to the mineralisation and at some distance downslope from it (Fig. 7a); the downslope anomaly is much broader and stronger. Detectable concentrations of arsenic weakly adsorbed on soils are confined to the vicinity of the suboutcrop of the mineralisation (Fig. 7b); the weaker of the two anomalies in soil air coincides with sites at which there is arsenic weakly adsorbed on soils. The interpretation placed on these findings is that one or more volatile species of arsenic occur both in soil air and weakly adsorbed on soils directly over the arseniferous

mineralization as a result the generation of trace quantities of arsenic gases during arsenopyrite oxidation. During oxidation, soluble arsenic species are also released into the groundwater and migrate downslope to a redox barrier where volatile arsenic species pass into the soil air. The absence of volatile arsenic adsorbed on the soil at the downslope location may be due to differences in either soil type or volatile arsenic species compared to those at the location above the suboutcrop of the mineralisation.

Antimony and bismuth have much lower abundances than that of arsenic (Table 2) and have attracted little interest as gaseous pathfinders. Boyle and Jonasson (1984) point out that antimony may occur as the gases stibine, dimethylstibine and other methylantimonials, but its primary dispersion halos in ore minerals tend to
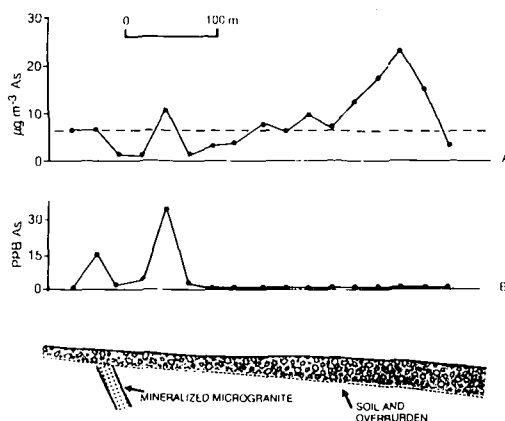

FIG. 7. Soil traverse over scheelite-arsenopyrite mineralised microgranite at Ballinglen, Ireland, showing: (a) arsenic in soil air; and (b) arsenic weakly adsorbed on soils.

be much more restricted in areal extent than those of arsenic. Although the contribution of bismuth to mineral exploration has been demonstrated (e.g., Plant *et al.*, 1989), theoretical considerations suggest that the natural occurrence of bismuth gases (such as bismuth hydride) may be discounted.

Conclusions

Through the processes of oxidation and radio-decay, ore minerals give rise to a number of metastable chalcogen gases. Their concentrations in the natural environment are extremely low, making them difficult to detect. One of their attributes, however, is their propensity for adsorption on soils. As a result of this, analytical problems associated with their detection are alleviated. Soils act as gas flux integrators, gas accumulators and convenient sample media.

Anomalous concentrations of several chalcogen gases have been detected over known mineral deposits, but patterns tend to be erratic and diffuse compared with those which arise through conventional geochemical dispersion. Gas migration pathways from source to surface are particularly poorly understood. There is ample evidence of, and speculation about, migration of gas precursors in solution in groundwater, preferential gas migration along conduits such as faults and fractures, and gas generation as a result of changes in near-surface soil drainage conditions. Thus, more research will be needed to establish the value and significance of these gases as pathfinders for concealed and blind mineral deposits.

References

Boyle, R. W. and Jonasson, I. R. (1973) The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. *J. Geochem. Explor.*, **2**, 251–96.

——— (1984) The geochemistry of antimony and its use as an indicator element in geochemical prospecting. Ibid. **20**, 223–302.

Card, J. W. and Bell, K. (1985) The relationship of soil ^{210}Po and ^{210}Pb geochemical dispersion patterns to uranium mineralization. Ibid., **23**, 101–15.

Dyck, W. (1984) Evaluation of the ^{210}Po method at the Midwest uranium deposit, northern Saskatchewan, Canada. Ibid., **20**, 85–92.

Henderson, P. (1982) *Inorganic Geochemistry*. Pergamon Press, 353 pp.

Hinkle, M. E. and Dilbert, C. A. (1984) Gases and trace elements in soils at the North Silver Bell deposit, Pima County, Arizona. *J. Geochem. Explor.*, **20**, 323–36.

—— and Kantor, J. A., 1978. Collection and analysis of soil gases emanating from buried sulfide mineralization, Johnson Camp area, Coschise Country, Arizona. Ibid., **9**, 209–16.

—— Ryder, J. L., Sutley, S. J., and Botinelly, T., 1990. Production of sulfur gases and carbon dioxide by synthetic weathering of crushed drill cores from the Santa Cruz porphyry copper deposit near Casa Grande, Pinal County, Arizona. Ibid., **38**, 43–67.

Jin Jun, Hu Zhengqing, Sun Xiangli, Zhang Maozhong, and Zhan Meidi (1989) Geochemical exploration in thick transported overburden, eastern China. Ibid., **33**, 155–69.

Kesler, S. E. and Gardner, M. (1986) Factors affecting sulfur gas anomalies in overburden. *J. Geophys. Res.*, **91**, 12,339–42.

—— Gerdenich, M. J., Steininger, R. C., and Smith, C. (1990) Dispersion of soil gas around micron gold deposits. *J. Geochem. Explor.*, **38**, 117–32.

Lakin, H. W., 1972. Selenium accumulation in soils and its adsorption by plants and animals. *Bull. Geol. Soc. Amer.*, **83**, 181–90.

Levinson, A. A. (1980) *Introduction to exploration geochemistry*. Applied Pub., 924 pp.

Lovell, J. S., Hale, M. and Webb, J. S. (1980) Vapour geochemistry in mineral exploration. *Mineral. Mag.*, **143**, 229–39.

Nicholson, R. A., Peachey, D. and Ball, T. K. (1988) Tests on use of sulphur gases in soils to detect hidden mineralization. *Trans. Instn. Min. Metall.*, **971**, B57–63.

Oakes, B. W. (1984) *Vapour geochemical pathfinders for oxidizing sulphide mineralization beneath exotic overburden*. Unpub. PhD thesis, Univ. of London, 350 pp.

—— and Hale, M. (1987) Dispersion patterns of carbonyl sulphide above mineral deposits. *J. Geochem. Explor.*, **28**, 235–49.

Plant, J. A., Breward, N., Forrest, M. D. and Smith, R. T., (1989) The gold pathfinder elements As, Sb and Bi—their distribution and significance in the southwest Highlands of Scotland. *Trans. Instn. Min. Metall.*, **98**, B91–101.

Rose, A. W., Hawkes, H. E. and Webb, J. S. (1979) *Geochemistry in mineral exploration*. Academic Press, 657 pp.

Ruan, T., (1982) *Some new approaches in vapour geochemistry*. Unpub. rep., Imp. Coll. Sci. Techl., London.

Taylor, C. H., Kesler, S. E. and Cloke, P. L. (1982) Sulfur gases produced by the decomposition of sulfide minerals; application to geochemical exploration. *J. Geochem. Explor.*, **17**, 165–85.

Watterson, J. R., Gott, G. B., Neuerburg, G. J., Lakin, H. W. and Cathrall, J. B. (1977) Tellurium, a guide to mineral deposits. Ibid. **8**, 31–48.