# VAPOUR DISPERSION OF MERCURY AND RADON AT CACHINAL, NORTHERN CHILE

**JAIME A. ARIAS** Inst. Invest. Geológicas. Casilla 10465, Santiago, Chile

**M. HALE** Applied Geochemistry Research Group, Department of Geology, Imperial College, London

**J.S. WEBB** Applied Geochemistry Research Group, Department of Geology, Imperial College, London

## RESUMEN

Se llevó a cabo un muestreo de gas del suelo y determinación, en el lugar, de Hg y Rn en Cachinal, en el norte de Chile, donde toda expresión geoquímica convencional de la mineralización de Ag en profundidad es obscurecida por la contaminación proveniente de desmontes y por la presencia de una cubierta de arenas y gravas transportadas. La respuesta geoquímica convencional en la parte superior de la roca fundamental está ausente, debido a la intensa lixiviación de Ag.

Niveles anómalos de Hg en gas del suelo ocurren sobre el sub-afloramiento aproximado de una veta en dos perfiles, pero, anomalías no relacionadas a mineralización conocida también se presentan en el área. La ocurrencia de solamente anomalías de Rn de escaso contraste, sobre la posición estimada de mineralización en un perfil y asimismo sobre roca fundamental, aparentemente no mineralizada, es atribuida a la ausencia de una clara asociación de U con la mineralización.

## ABSTRACT

Soil air sampling and on-site determination of Hg and Rn carried out at Cachinal, northern Chile, where any conventional geochemical expression in the soil of Ag mineralization at depth is obscured by mine-dump contamination and a cover of transported sands and gravels. A conventional geochemical response at the top of bedrock is absent due to intense leaching of Ag. Anomalous levels of Hg in soil air occur over the estimated suboutcrop of a mineralized vein along two traverses, although anomalies unrelated to known mineralization also occur within the area. The occurrence of only low contrast Rn anomalies over the estimated position of mineralization on one traverse and also over apparently non-mineralized bedrock, is attributed to the absence of a distinct U association with the mineralization.

## INTRODUCTION

Cachinal is a former silver-mining area located approximately 100 km northeast of Taltal at 69° 30' W and 25°00' S, in the Atacama Desert of northern Chile. The district is some 2,700 m above sea level. Accurate climatic data for Cachinal are not available, but average maximum daily temperatures are typically 13 to 15°C in July and 20 to 21°C in January. Rainfall is rare, and averages only a few millimetres per year. Natural vegetation is almost totally absent. There has been no human habitation in the district since the cesation of mining almost 50 years ago.

*Revista Geológica de Chile N° 8, pp 3-12, 7 figs . 1979.*

## GEOLOGY

The geology of the Cachinal district is described by Chong (1976). Stratified Cretaceous and Tertiary volcanic rocks rest unconformably on Jurassic marine sediments. The volcanics comprise a basal series of rhyolites and dacites, intercalated with sedimentary breccias and sandstones, and an upper volcanic series of andesites and dacites. Hypabyssal domes, necks and dykes, possibly of Miocene age, intrude the stratified series. These subvolcanic intrusives are mainly porphyries of rhyolite composition and sub-volcanic granites. Hydrothermal alteration affects the rocks, especially the acid volcanics and granites, which have undergone feldspar argillization.

Sulphide mineralization occurs as a system of veins which bifurcate and coalesce along the strike of a major north-south structure which runs for at least 2.5 km. The richest mineralization is found in intensely brecciated rhyolite porphyries. The brecciated ore zones are reported by Greiner (1978) to be up to 10 m wide, and Kuntz (1928) states the ore zone is 20 m wide at one locality. According to Moreno (1974), individual ore shoots are up to 1 m wide. Chong (1976) states that the primary mineralization comprises sphalerite, argentiferous galena, chalcopyrite, pyrite, tennantite and ennargite. The primary mineralization occurs at depths of 120 m or more. The maximun depth of mineralization recognized by Kuntz (1928) is 320 m. A leached zone of unspecified thickness occurs directly beneath the overburden. In the oxidized zone, Chong (1976) reported secondary minerals including covellite, pyrolusite, magnetite, hematite and traces of uraninite.

The area is largely covered by colluvial overburden 2 to 15 m in thickness. Bedrock is exposed on a small hill, which rises some 25 m above the pediment surface, and by old mine workings. Consequently, the detailed bedrock geology of the area is not well known except in the vicinity of these exposures.

## MINING HISTORY AND CONTAMINATION

Chong (1976) reported that the veins at Cachinal were exploited from 1850 to 1930, and that annual production averaged 72 t of silver. Exploitation was via a series of shafts of which the largest were the Arturo Prat shaft situated on the small hill in the area, and the Esperanza shaft some 800 m further north. Around these shafts and smaller ones between them are large rock dumps estimated to contain 76 t of silver. A further 30.000 t of ore of unspecified grade remains in situ. When mining was in progress the ore was refined at Cachinal, and there is a tailings dump in the south of the area.

The large dumps of mineralized rock are an obvious source of contamination. Even apparently undisturbed ground surfaces are likely to have a litter of debris derived from collapsed dump material, or a fine dusting of windborne material blown from the dumps. The tailings dump in the south of the area may be a source of similar contamination.

## ROCK AND SOIL GEOCHEMISTRY

Hand specimen rock samples from mine dumps and prospect trenches in the vicinity of proposed soil and soil air sampling traverse lines were collected and analyzed for Ag, U and Hg. Silver was determined by flame atomic absorption spectrophotometry following sample digestion in a mixture of hot nitric and perchloric acids. Uranium was determined by neutron activation. Mercury was determined by cold vapour flameless atomic absorption spectrophotometry following sample digestion in hot nitric acid and reduction of $Hg^{+2}$ in solution to volatile Hg.

A total of 45 rock samples were analyzed for Ag, and results ranged from 0.2 ppm to 540 ppm; the high results were from samples collected from mine dumps. The same 45 samples contained

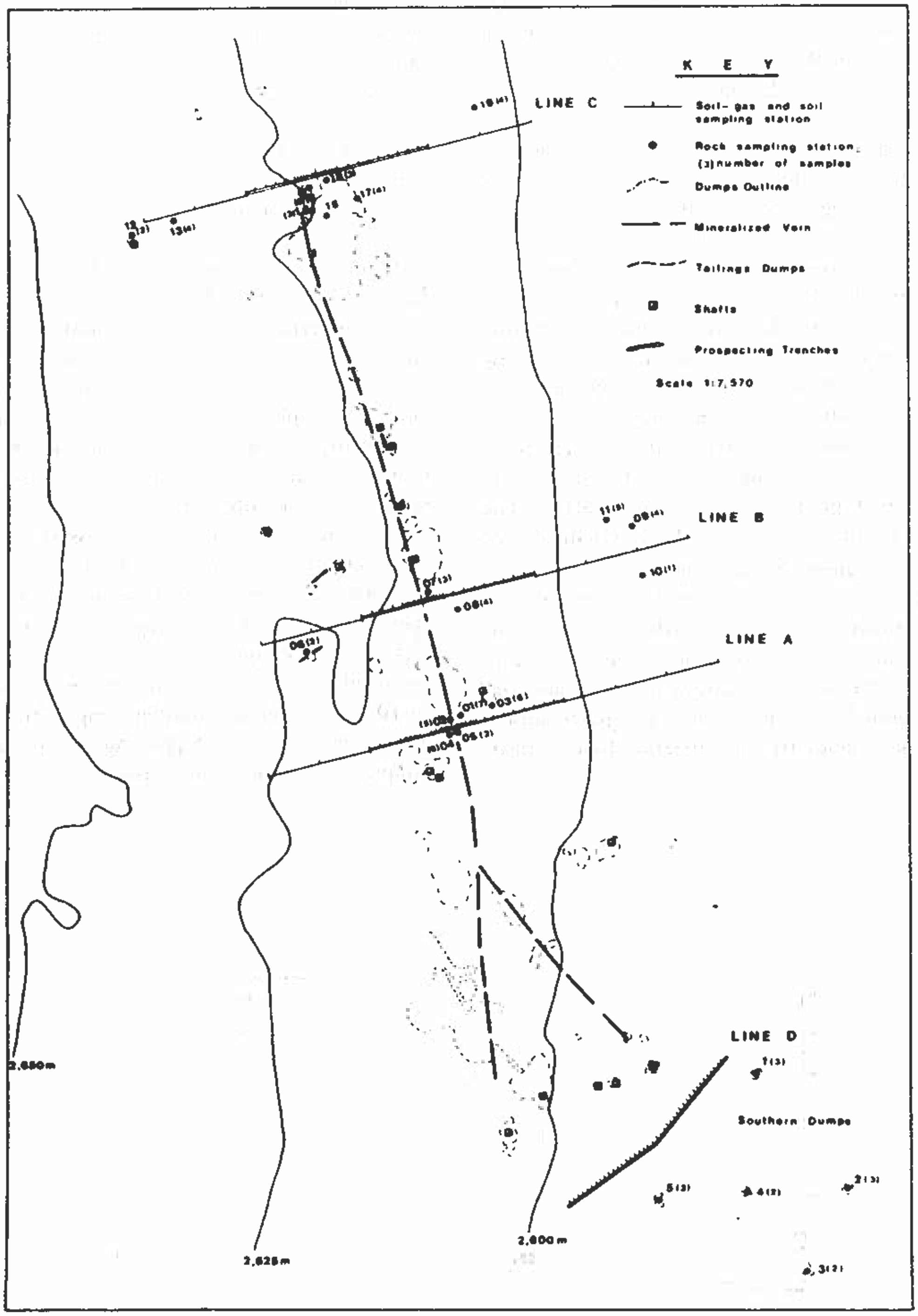

Fig. 1 Location of Rock, Soil and Soil Gas Sampling Stations at Cachinal

between 1.2 and 8.7 ppm U, with some limited correlation between high levels of Ag and high levels of U. Clearly the U contrast between mineralized and non-mineralized specimens is much poorer than the Ag contrast. Mercury was determined in 21 of the 45 specimens, and results ranged from 16 to 2,225 ppb, reflecting a contrast comparable with that seen for Ag.

Acid igneous silicate rocks contain relatively little Hg, for example Jonasson and Boyle (1972) state the average Hg content of andesites is 66 ppb. No mercury minerals have been reported at Cachinal, and therefore the higher concentrations of Hg are thought to occur within the lattices of sulphides such as sphalerite and galena; Jonasson and Boyle (1972) give the normal range of Hg contained in sphalerite as 0.1 to 200 ppm, and in galena as 0.04 to 70 ppm. Average U contents of acid igneous rocks, reported by Rich et al. (1977) range from 2 ppm in diorites and quartz diorites to 5 ppm in rhyolites and dacites. The range of U concentrations in the 45 Cachinal rock specimens is therefore not substantially different from the U content typical of the types of acid igneous rocks that constitute the host rock for the mineralization. Nevertheless, reported occurrences of traces of uraninite with the mineralization suggested that the value of Rn geochemistry as a possible guide to mineralization be investigated.

To ascertain the conventional geochemical expression of the mineralized veins at or near the surface, a soil sampling line, traverse A, was laid out running approximately east-west over 880 m (Figure 1). At the extremities of the traverse the sample site interval was 100 m, closing to 20 m then 5 m over the zone suspected to include the mineralized veins. The intersection of the traverse line with the mineralized zone was chosen to coincide with gaps between mine dumps. This maximized the degree of confidence with which the position of the mineralization could be predicted, and minimized as far as possible contamination from dumps. At each of 40 sites, three samples from the vertical profile were obtained using a truckmounted auger drill. Overburden samples were taken from 0 to 0.5 cm and from 0.5 cm to 5 cm, and samples were also taken from a depth of 3 m, or top of bedrock, whichever was less. Except in the extreme east of the traverse, these latter samples were usually bedrock.

The samples were dried, if necessary, and sieved with retention of the -75 μm fraction. Samples were analyzed for Ag by flame atomic absorption spectrophotometry following a hot nitric acid digestion. The samples taken from 0 to 0.5 cm in the overburden have Ag contents in the range 1.9 to 106 ppm. The overburden samples from 0.5 to 5 cm contain 0.8 to 61 ppm Ag. In both types of sample the highest values form a broad zone in

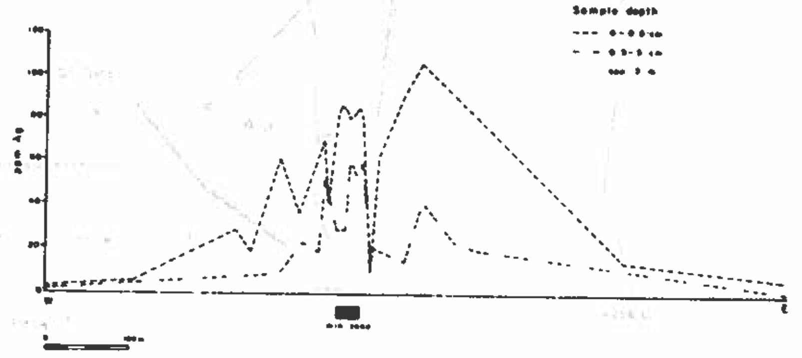

Fig 2. Traverse A; Ag in overburden and bedrock

the vicinity of the suboutcrop of the veins and the mine dumps. The Samples from 3 m all contain less than 2 ppm Ag (Figure 2).

The uniformly low Ag concentrations in samples taken mainly from bedrock at depths of up to 3 m beneath the surface fail to indicate the position of the suboutcrop of the mineralized veins. This is attributed to intense leaching of Ag from the upper sections of the veins. Exceptionally high levels of Ag in the overburden must be due to contamination from mine dumps or former mining activity.

## VAPOUR DISPERSION AT CACHINAL

Attempts to measure Hg and Rn in soil air were adopted in order to utilize vapour dispersion patterns in detecting the presence of sulphide mineralization at depth, beneath exotic overburden and a leached zone.

Radon is a member of the radioactive decay series of $U^{238}$. Most of the intervening members of the series are relatively immobile, so that Rn can be considered to be generated in the immediate vicinity of $U^{238}$. Radon is an inert gas with a half life of 3.8 days, and thus Rn decays to 1% of its initial concentration in 20 days. This is a sufficiently long time for a Rn dispersion halo to form around its radiogenic parent. The traces of lattices is greatly accelerated by their physical and chemical breakdown.

Mercury comprising a minor constituent within the lattices of sulphide minerals can be mobilized through the oxidation of the host sulphides. Native Hg is soluble in water, can migrate in groundwater, and can travel as a gas in the aerated pore space of rock and soil. Jonasson (1970) and Evans (1972) refer to the migration of Hg as volatile organic compounds, but this form of migration has been studied very little.

Rodon and Hg vapour within mineral deposits will migrate by diffusion and mass flow, and thereby reach the surface. Zones of maximun porosity and permeability provide pathways along which vapour dispersion is preferentially promoted. Mercury is prone to adsorption by clay minerals (common constituents of hydrothermal alteration mineral assemblages), but within porous rocks and overburden materials an equilibrium

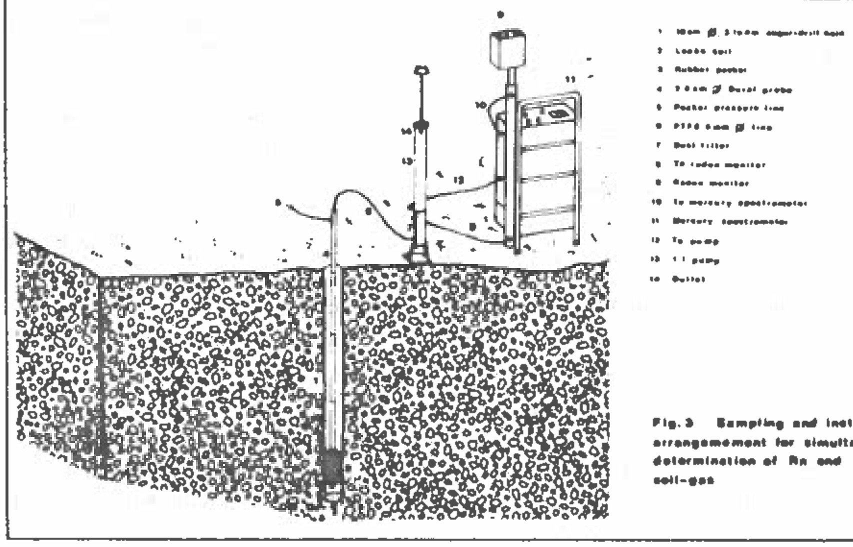

Fig. 3 Sampling and instrumental arrangemement for simultaneous determination of Rn and Hg in soil-gas

U at depth in the Cachinal mineralization will produce radiogenic daughter products, including Rn which might be capable of migrating to the surface. Radioactive decay proceeds spontaneously and independently of physicochemical conditions, although the escape of Rn from mineral between adsorbed and vapour-state Hg is presumably reached. Koksoy and Bradshaw (1969) found that Hg vapour dispersion was fundamentally controlled by bedrock fracturing and alteration. Inert Rn is not adsorbed by minerals with which it comes into contact.

The concentrations of Rn and Hg reaching the near-surface bedrock and overburden pore space can be measured in the field using portable instruments, and this was done at Cachinal. Mercury in soil air was determined using a Scintrex HGG-3 portable cold vapour atomic absorption spectrophotometer (Figure 6). This instrument, described in detail by Robbins (1972), has a specific response to Hg based on the Zeeman modulation of the signal from the hollow cathode lamp, and a limit of detection of 40 pg Hg in a 250 ml sample cell. Absorption in the cell is measured as a photomultiplier tube response in millivolts, which is proportional to the concentration of Hg. Calibration in the field is obtained by injecting into the instrument cell known amounts (100 to 500 $\mu$l) of saturated Hg vapour using a microlitre syringe. The Rn content of soil air was measured using an Ekco radon monitor (Figure 7), which has been described by Miller and Loosemore (1968). The principle upon which the instrument operates is to count the rate at which alpha particles generated by the radioactive decay of Rn in the soil air sample impinge upon a zinc sulphide phosphor. Count times of 60 seconds were usually satisfactory for obtaining reproducible Rn measurements at Cachinal. In-field calibration of the Rn monitor is made using $Am^{241}$ as a source of alpha particles.

Soil air sampling sites were concentrated along two traverse lines, running approximately east-west. Both traveses were sited on apparently undisturbed and minimally contaminated ground, and positioned to intersect the estimated subcrop of the mineralized veins between old shafts. In this way the position of a potentially mineralized zone could be delineated with some degree of confidence. Traverse A was the same line as that used for soil sampling, and the same 40 sample sites were used. Traverse B ran parallel to traverse A 170 m to the north, and comprised 35 sample sites over 840 m with a sample site distribution similar to that on traverse A. Additional samples were also taken: some to the north and to the south of the area in which the shafts are sited, where any continuation of the mineralized veins was thought improbable; and some further to the east of the former mining area, where there was still less likelihood of mineralization.

At each sample site, an auger hole 10 cm in diameter was sunk to a depth of 3 m or top of bedrock (whichever was less) using a truck mounted drill. After allowing several days for the restoration of soil air equilibrium in the overburden and bedrock pore spaces around the auger hole, a soil air sample was obtained using a probe developed by Lovell (in prep.). The probe consisted of several 1 m lengths of duraluminium tubing of 2.5 cm external diameter. The individual sections had threaded ends to allow a probe up to several metres in length to be assembled. The lowermost section had an inflatable rubber packer fitted coaxially around the tube along part of its length. For sampling, the rubber packer and probe were lowered into the hole to within 5 cm of the bottom. The packer was then inflated using a hand-pump, isolating the bottom of the hole. Using a 1 litre hand-pump, a soil air sample was pumped from the lower part of the hole through the hollow probe (Figure 3), and then via Teflon tubing past a cotton wool dust filter and into Hg and Rn meters connected in series.

Teflon tubing and a cotton wool dust filter were selected following laboratory experiments which demonstrated that these did not absorb Hg vapour. The Rn monitor was adapted for in-series use with the Hg spectrophotomer by enclosing the Rn monitor probe (which in conventional operation is inserted in a hole in the ground) in an aluminium sheath. An airtight seal between the probe and the sheath was obtained by a leather washer smeared with silicone grease located above the intake perforations of the probe. The soil air sample was pumped through the sheath, and hence made contact with the alpha particle detector as in normal operation.

A soil air sampling depth of approximately 3 m was chosen to minimize possible difficulties in obtaining reliable Hg and Rn measurements due to variations in atmospheric temperature and pressure and sample dilution with atmospheric air. McCarthy (1972) pointed out that daily changes in temperature could produce increases in the Hg content of air through soil warming. However, in-hole temperatures measured at Cachinal were generally about 17°C. McCarthy (1972) also indicated that atmospheric pressure changes appeared to influence near-surface soil air Hg levels, possibly due to atmospheric pumping, but sampling from a depth of several metres eliminated this problem. Variations in the Rn content of near-surface soil air due to atmospheric pressure changes were reported by Schroeder et al. (1965), who also stated that these effects were not noticeable at depths of 1 to 3 m below the surface. Entrainment of atmospheric air into soil air samples can occur when several litres of soil air are extracted from the pore space of shallow soils, but this problem is not encountered when samples are drawn from 3 m.

Using at Cachinal the field equipment described, the first litre of soil air pumped during sampling comprised air from the base of the auger hole plus the dead volume of the tubing, and was discarded. A series of 0.5 l samples were then extracted from the soil pore space around the base of the hole, and their Hg and Rn contents determined. The most reliable Hg results are considered to be those obtained after discarding a further 1 litre of soil air, while satisfactory Rn results were obtained after discarding only a further 0.5 l.

## RESULTS AND DISCUSSION

The 75 Rn measurements made along traverses A and B constitute a lognormal population, with values in the range 1 to 41 cpm.

Three anomalous values occur above a threshold set at 35 cpm on the basis of the population mean plus two standard deviations. The anomalies comprise measurements of 41 and 40 cpm at sites within the mineralized zone on traverse A, and a measurement of 40 cpm west of the mineralized zone on traverse B (Figures 4 and 5).

Of the 75 Hg measurements on traverses A and B, most appear to constitute a normal population with Hg levels in the range 2 to 8 ng/l. This is interpreted as the background population, and its upper limit provides a threshold of 8 ng/l. Two higher measurements that do not form part of this are clearly anomalous. The stronger anomaly is 19.8 ng/l Hg from a site over the mineralized zone on traverse A, and the other is 12.8 ng/l from a site over the mineralized zone on traverse B (Figures 4 and 5).

Both of the Hg anomalies and all but one of the Rn anomalies on traverses A and B were found in the zones of the traverses beneath which mineralization probably occurs. Anomalous levels of Hg and Rn were not found in all samples taken over the mineralized zones, and anomalous Hg measurements were not coincident with Rn anomalies. These factors do not necessarily detract from the significance of the anomalies. Varying bedrock permeability, perhaps related to fracture

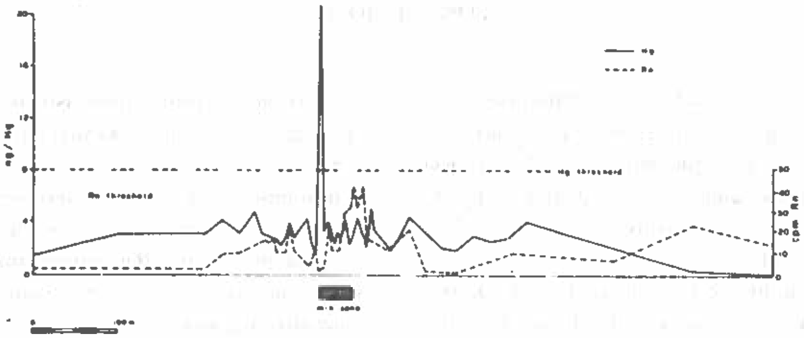

Fig 4 Traverse A, Hg and Rn in soil air

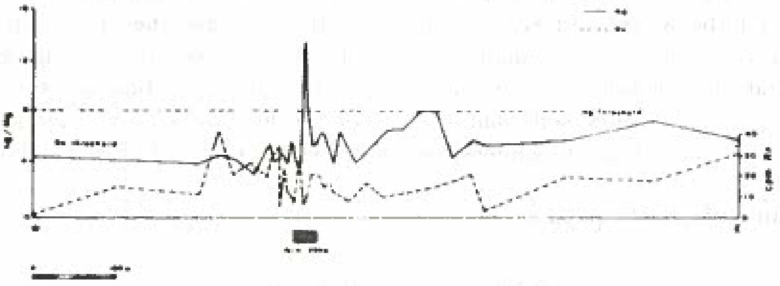

Fig 5 Traverse B, Hg and Rn in soil air

patterns, might largely direct vapour migration along particular channelways from depth into the soil pore space, producing localized and sometimes intense anomalies rather than diffuse haloes.

The non-significant Rn anomaly of 40 cpm in the western sector of traverse B was the highest Rn value obtained from all sites at Cachinal except those over the mineralized zone on traverse A. However, some of the additional sample sites to the north and south of the former mining area also yielded high concentrations of Hg, with a maximun of 20.9 ng/l. No extensions of the mineralized veins into the areas in which these samples were taken have been postulated; indeed Kuntz (1928) considered it unlikely that important mineralization occurred north of the Esperanza shaft (Figure 1). It seems most probable that high Hg levels in the north and south of the area are non-significant anomalies, but the possibility that they reflect some strike continuation of known mineralization cannot be excluded. The additional soil air samples taken to the east of the former mining area contained less than 1 ng/l Hg.

## CONCLUSIONS

There is no conventional soil geochemistry expression of the Ag mineralization at Cachinal. The exotic overburden is contaminated with material from mine dumps, and the top of the bedrock, usually found at approximately 3 m below surface is intensely leached.

Clear contrast in Hg content of host rock and mineralized rock specimens at Cachinal was successfully exploited by the detection of soil air Hg anomalies in the pore space of near-surface leached bedrock and overburden above known mineralized zones. Some high Hg values beyond the established strike extent of the mineralized veins may be related to more mineralization but equally may be false anomalies.

Uranium analysis of mineralized rock specimens from Cachinal demonstrated that uraninite reported in the veins was sparsely distributed and/or present in extremely low concentrations. Poor or non-existent U contrast between host rocks and mineralized rocks was reflected in soil air samples by a single normal Rn population, within which two anomalous values were from soil air over the mineralized zones, but one was clearly a false anomaly unrelated to mineralization.

This study shows that the principle of vapour migration migth be used to advantage in prospecting the arid regions of northern Chile for undiscovered mineralization concealed beneath exotic overburden and/or an intensely leached zone, and in exploring for extensions to known mineralization in areas contaminated by mine waste.

## ACKNOWLEDGEMENTS

The research project into the applications of vapour geochemistry to mineral exploration of which this study forms a part was sponsored in Chile by the Instituto de Investigaciones Geológicas and at the Applied Geochemistry Research Group, Imperial College, London, by a Mineral Industries Research Organization syndicate comprising Charter Consolidated Limited, Consolidated Gold Fields Limited, RTZ Services Limited and Union Corporation Limited. The support of these organizations and their permission to present this paper is gratefully acknowledged. The authors are indebted to ENAMI for permission to work at Cachinal and the valuable assistance of Sres. G. Greiner and P. Egaña in the field. The Ekco Rn monitor was very kindly loaned by the Institute of Geological Sciences, London.

## REFERENCES

CHONG, G. 1976. Antecedentes geológico-mineros del distrito Cachinales de la Sierra, II Región, Antofagasta. SERPLAC-Antofagasta, Unpub. Report.

CHONG, G.; MORENO, H. 1974. Informe del reconocimiento de yacimientos argentíferos y auríferos de la II Región Antofagasta. Unpub. Report Instituto de Investigaciones Geológicas, Santiago.

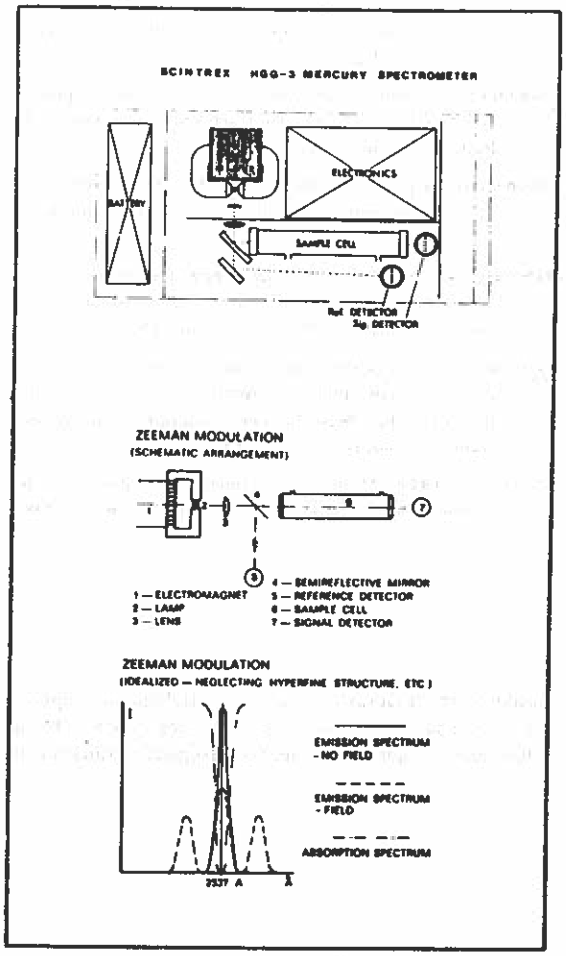

Fig. 6 Mercury Spectrometer Layout and Working Principle

Radon Monitor Controls and Sectional View

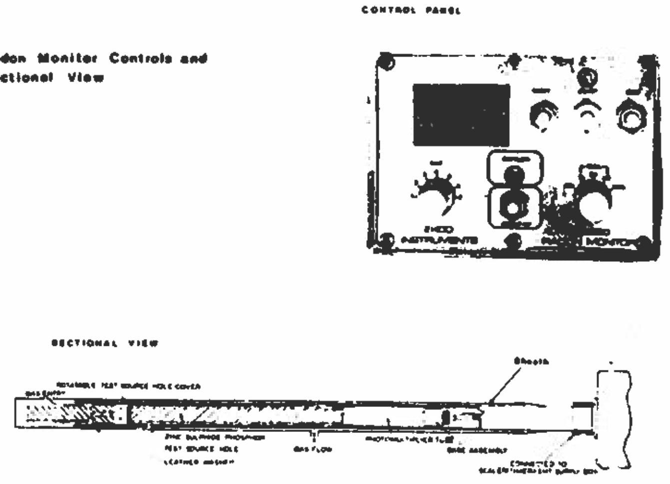

Fig. 7

**EVANS, D.S. 1972.** Secondary dispersion of Hg and associated elements at Keel, Eire. Unpub. DIC Thesis, Imperial College, London.

**GREINER, G. 1978.** Antecedentes de evaluación geológica distrito argentífero Cachinal de la Sierra, II Región. Unpub. Report ENAMI.

**JONASSON, I.R. 1970.** Mercury in the natural environment; a review of recent work. Geol. Survey of Can., Paper 70-57, 1970.

**JONASSON, I.R.; BOYLE, R.W. 1972.** Geochemistry of mercury and origins of natural contamination of the environment. CIM Bulletin Jan. 1972.

**KOKSOY, M.; BRADSHAW, P.M.D. 1969.** Secondary dispersion of mercury from cinnabar and stibnite deposits. West Turkey. Colorado Sch. Mines, Quart., V. 64, N°1, p. 333-356.

**KUNTZ, J. 1928.** Monografía Minera de la Provincia de Antofagasta. SONAMI ed., Santiago, Chile, 1928.

**LOVELL, J.S.** (In preparation). Applications of vapour geochemistry to mineral exploration. Unpub. PhD Thesis, University of London.

**McCARTHY, J.H.J. 1972.** Mercury vapor and other volatile components in the air as guides to ore deposits. J. Geochem. Explor., V. 1, p. 143-162.

**MILLER, J.M.; LOOSEMORE, W.R. 1968.** Instrumental techniques for uranium prospecting. Uranium Exploration Handbook, IMM London 1968, p. 135-148.

**RICH, R.A., et al. 1977.** Hydrothermal uranium deposits. Devs. in Econ. Geology 6, Elsevier, Amsterdam.

**ROBBINS, J.C. 1972.** Zeeman spectrometer for measurement of atmospheric mercury vapour. IMM London, p. 315-323.

**SCHROEDER, G.L.; KRANER, H.W.; EVANS, R.D. 1965.** Diffusion of radon in several naturally occurring soil types. Journ. Geoph. Res., V. 70, N°2, Jan. 1965, p. 471-474.

**NOTA DEL EDITOR.** El presente trabajo fue expuesto en las sesiones del II Congreso Geológico Chileno realizado en la ciudad de Arica, Chile, entre los días 6 y 10 de Agosto de 1979. La autorización para su publicación en la Revista Geológica de Chile, fue otorgada a solicitud del Editor.