

U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

CHIM – An Electrogeochemical Partial Extraction Method:

An Historical Overview

by

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Open-File Report 97-92

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Introduction

The CHIM electrogeochemical method was developed in the former USSR during the late 1960's and early 1970's at the All-Union Research Institute of Exploration Technology, VITR, located in Leningrad (now St. Petersburg) Russia. The acronym CHIM is derived from the Russian Words Chastichnoe Iz vlecheniye Metallov which mean "partial extraction of metals". The concept of CHIM is straight forward; a dc electrical current is introduced into the ground through special electrolyte filled ion collection electrodes. The action of the electrical current drives ions present in the soil into the collection electrode. Cations go to the cathode and anions to the anode. The electrolyte into which the soil ions are driven then constitutes the geochemical sample, which is analyzed for elements of interest. Because, ideally, the elements that are driven into the collection electrode are only those present as dissolved and ionized species in the soil moisture, a CHIM extraction is a weak partial extraction of soil components, as the name suggests.

The CHIM method has had extensive development in the former USSR, where it has been applied to minerals and oil and gas exploration. Significant development of the method has occurred, and is continuing, in the Peoples Republic of China, also for minerals and oil and gas exploration. More recently western minerals exploration groups have begun to take an interest in the CHIM technology. The U.S. Geological Survey began CHIM research in 1989. USGS research has been directed at understanding the basic process of CHIM extractions and determining its applicability to minerals exploration, mineral resource assessment, and environmental monitoring.

Russian researchers claim that the principal advantage of the method is its ability to detect geochemical anomalies over mineral deposits buried at depths of 100's of meters where conventional geochemical soil methods fail. Another advantage of CHIM apparent from initial USGS research was that as an in situ extraction it would eliminate time consuming soil preparation stages. It also appeared to us that CHIM was a means of sampling moisture in relatively large volumes of soil. The larger volume would improve sampling statistics and enhance the concentration of ions in the extract. Because extensive USGS research had demonstrated the effectiveness of partial extractions in minerals exploration, we believed CHIM, defined by the Russians as a method of partial extraction, deserved investigation. CHIM's obvious disadvantage is the logistical problem of supplying high voltage electrical power to the electrodes.

The purpose of this report is to provide an historical overview of research and

development of CHIM for use in exploration. Interest in the method has expanded throughout the world, yet much of the literature is not readily accessible in English. We hope the overview in this report provides English readers sufficient information to make decisions on when or how to use the method.

I. Russian Development

A. Sokolova's Early Work

The first published article describing an electrogeochemical extraction from soils for mineral exploration purposes appears to be by Sokolova (1967) who calls her technique an electrochemical method. This technique was developed at the Sverdlovsk Mining Institute over several years prior to the publishing of the 11 page article by Sokolova (1967). This early variation of the CHIM method had distinct field and laboratory variants.

In the laboratory variation, an electrochemical cell, figure 1, is filled with screened soil taken from a 0.5 to 1.5 kg soil sample. Sokolova calls this an electrolytic cell. The < 0.5 mm screened soil fraction is used to fill the chamber, which contains brass electrodes at the top and bottom. Typically, a constant DC current of 0.2A is passed through the cell for 20 minutes (a current density of 7 mA/cm²). A small amount of soil, taken near the anode and cathode ends of the cell, figure 1, constitutes the electrochemical sample which is then analyzed for appropriate ions. Sokolova mentions or shows data for SO₄²⁻, HCO₃⁻, F⁻, Ca²⁺, Mg²⁺, Na⁺, and K⁺. In the field version, 4 to 5 iron electrodes (pairs?) are placed in shallow holes in the ground where a DC current of 0.2A is used for a period of 30 minutes to accumulate ions in the vicinity of the electrodes. Soil samples are then taken from a radius of 4-5 cm from the electrodes.

Besides these electrochemical "extractions" Sokolova also makes a water extraction of an unprocessed soil sample which is used to normalize the electrochemical data. Her data are then presented as electrochemical anomalies, A_{ec}, defined by,

$$1. A_{ec} = \frac{C_{ec}^i - C_{eH2O}^i}{C_{eH2O}^i} \times 100\%$$

where C_{ec}^i is the concentration of a particular ion, i, in the electrically processed soil, and C_{eH2O}^i is the concentration of the ion, i, in the water extract.

The focus of Sokolova's report (1967) is on the sulfate ion. She shows results for four sulfate ion surveys over sulfide deposits, and laboratory studies of various sulfate-bearing soils comparing extractions using platinum and graphite anodes. Figure 2, adapted from Sokolova (1967) shows sulfate ion results over the Abey-Saz Cu-Zn-Pb deposit in the Bashkir Autonomous S.S.R. In this example the sulfate anomaly defined by equation 1 corresponds to the surface projection of ore bodies and reaches a maximum of 350%.

Although much is unexplained in this early paper, it was a major step in trying to exploit

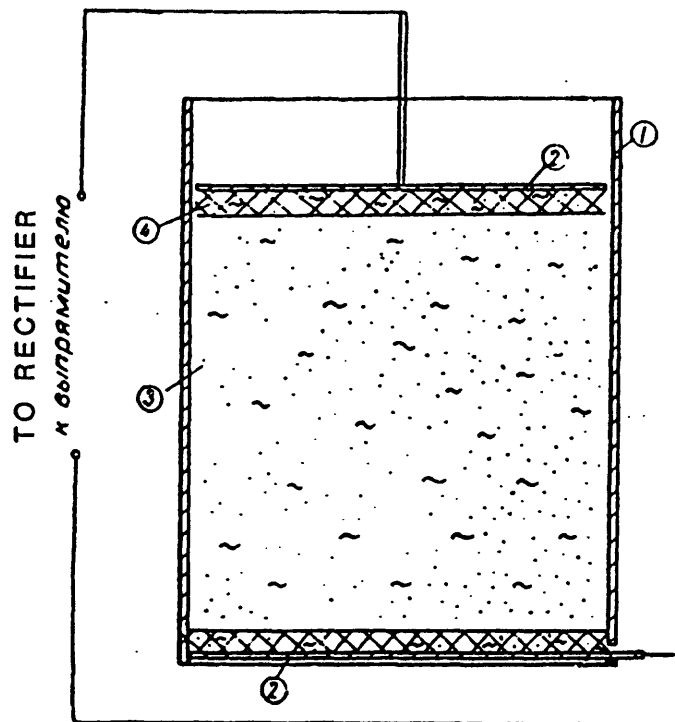


Рис. 1. Схема электролитической ячейки:
 1 — стакан из винипласта; 2 — пластинчатые латунные электроды;
 3 — почвенные отложения, фракция <0.5 мм; 4 — участки пробы,
 отбираемые после пропускания тока для анализа

Schematic of Sokolov's "electrolithic" cell. No scale indicated.

1. Plastic container. 2. Brass plate electrode. 3. Soil sample, fraction < 0.5mm. 4. Fraction of soil sample selected for analysis after passing current.

Figure 1. Laboratory electrochemical cell used by Sokolova (1967) to concentrate anions and cations from a soil sample into the vicinity of metal anodes and cathodes. An analogous field method was also used. More recently a variation of this technique has been patented by probstein and others (1991) for remediation of hazardous waste sites.

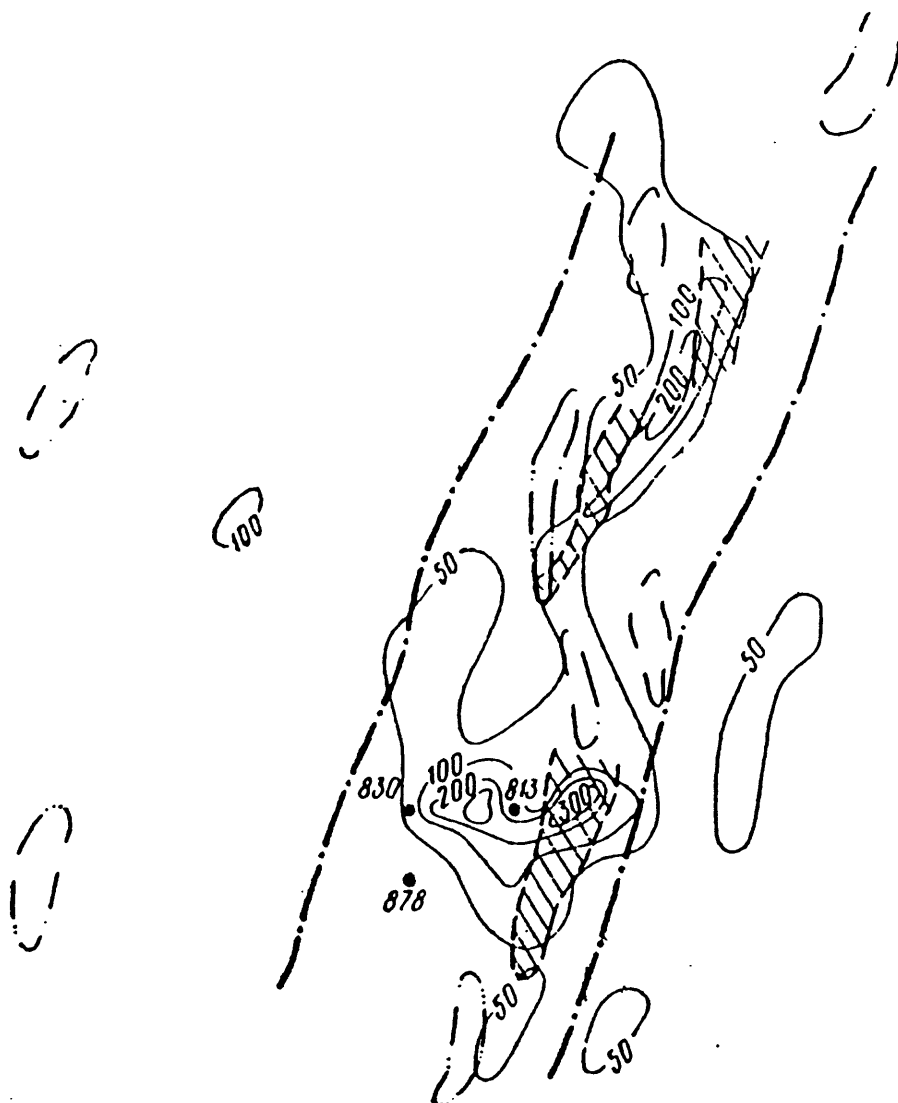


Рис. 4. Результаты исследований на участке Абей-Саз:

1 — проекция выхода некоторых рудных тел на дневную поверхность; 2 — тектоническая зона с повышенным содержанием сульфидов; 3 — аномалия метода изолиний; 4 — изолинии интенсивности электрохимических аномалий по сульфат-иону; 5 — изолинии содержания сульфат-иона в исходных пробах; 6 — аномальные содержания Cu, Zn, Pb в почве; 7 — рудные скважины

Figure 2. Results of a CHIM-like soil electrochemical extraction over the Abey-Saz deposit in the Bashkir Autonomous S.S.R., adapted from Sokolova (1967). Hachured area is the surface projection of ore; heavy dashed line is a tectonic zone with increased sulfide content; dashed line shows soil anomalies of Cu, Zn, and Pb; solid contours show electrochemical anomalies for sulfate.

the use of electromigration to concentrate and extract ions from soils for exploration purposes. It is also significant because of the focus on anions, a subject that would be neglected in published field studies to follow. Sokolova does not appear to be properly recognized as the founder of this technology. Although Shmakin (1985) does credit her for this pioneering work, numerous papers from the Scientific Production Organization (NPO), "Geotekhnika", (now NPO "Rudgeofizika"; NPO comes from *Nauchsso - Proizvodslvennoye Qb'edineniye*) fail to cite her in their work. No additional publications by Sokolova have been found on this subject.

B. Ryss and Goldberg's CHIM Work at Rudgeofizika

The scene shifts to Leningrad (now St. Petersburg) and the All-Union Research Institute of Exploration Technology, VITR, (*Vsesoyuznyy Nauchno-Issledovatel'skiy Institut Metodiki i Tekhnika Razvedki*), a part of NPO. The CHIM method, proper, was developed at VITR, principally by two individuals, Yuri Samuilovich Ryss (born 1928, died 1993) and Isaiah Solomonovich Goldberg (born 1929 -). Dr. Ryss was a geophysicist working principally in the area of electrical methods who developed an interest in electrogeochemical processes in the 1960's. Dr. Goldberg's background is in mineral genesis and mineral assessment. In 1965, he began studies of natural electrical processes and electromigration. In 1965 Drs. Ryss and Goldberg published a paper titled "Secondary mineral formation under the action of natural electrical fields of sulfide deposits" (Ryss and others, 1965); followed by Goldberg's paper (1969) on ion mobility in solutions in porous media. In his paper, Goldberg (1969) reports relatively high ion mobilities measured on laboratory samples of granite and polymict sand, with some mobilities an order-of-magnitude higher than dilute solution mobilities given in electrochemical texts. For these tests the rock or sand samples were saturated with solutions of Na_2SO_4 , NaCl , Na_2CO_3 , or MgSO_4 , ranging in concentration from 0.01M to 1.0M. In general, anomalous mobilities were reported for tests made with the 1.0M solutions. In the conclusions to this paper, Goldberg states that the increased ion mobility with high concentration in porous systems has vital theoretical and practical meaning. He further suggests that, over deposits showing a self potential field, the natural electrical field coupled with the high mobility may explain the presence of a geochemical halo. These high mobilities reported by Goldberg, and others to follow with VITR, may in part explain the statements and impressions in their CHIM papers that the method would draw ions from large distances.

Next, the seminal paper on CHIM proper was published by Ryss and Goldberg in 1973, titled The method of partial extraction of metals (CHIM) for exploration of ore deposits. It is in this paper where the acronym CHIM is first given, derived from the Russian words *Chastichnoe Izvlechenniye Metallov*, literally meaning partial extraction of metals. The last part of this paper, that which shows field results, has been translated in Bloomstein (1990).

The conceptual basis of the CHIM method is given in the first section of the paper. Ryss and Goldberg proposed using an electrolyte-filled electrode, that when placed on the ground and connected to a source of dc current, would act as a collector of ions moving from the earth into the electrode as a result of the current. This electrode was called an element receiver (*elementopriyemnika*, EPR). In order for electrical current to flow, and ions to enter the EPR,

galvanic contact to the earth was made by means of porous ceramic or parchment paper semi-permeable membranes in the EPR base. The membranes had to be sufficiently impermeable that little fluid would be lost due to hydrodynamic flow when the EPR was filled with electrolyte. Ryss and Goldberg (1973) give no illustration of an EPR, but illustrations of Russian designs of a ceramic and plastic body/parchment EPR, from later reports, are shown in figure 3. Electrolyte volume for the EPR was typically in the range of 50 to 100 cm³.

Although anion collection is occasionally mentioned, Rudgeofizika development focused on cation collection. As cation collectors, the EPR used pure graphite or titanium cathodes to make contact to the solution. Such cathodes are inert to the reduction processes occurring at the metal/solution interface. However, during operation the reduction occurring at the inner metallic electrode generates hydroxyl (OH⁻) ions that build up within the EPR. Ryss and Goldberg (1973) recognized the problem presented by OH⁻ buildup in the cathode EPR. The OH⁻ present in the EPR not only could precipitate many important cations collected from the soil within the EPR, but the current would migrate the OH⁻ out of the electrode into the earth. The resultant higher pH in the soil beneath the EPR would also precipitate important cations in the soil, thus preventing their collection. The remedy given by Ryss and Goldberg (1973) is to use acid as an electrolyte within the EPR. Typically nitric acid was used, in part because nitrates of most metals are soluble.

In this early paper Ryss and Goldberg (1973) also suggest that, during a CHIM extraction, electrochemical reactions on sulfide minerals associated with an ore deposit would solubilize metals that could then be collected. Use of electrolytic dissolution produced by a CHIM extraction current on a blind deposit at 100 meters depth, and migration of the ions produced to the surface, would require very large ion mobilities. The USGS does not believe direct extractions from great distances are practical.

Ryss and Goldberg (1973) also develop formulas for the time τ that an ion will travel a distance, h , in the earth, based on a constant electric field, E , and for a point source of current. For the constant electric field they give:

$$2. \quad \tau = \frac{h}{mE} = \frac{h}{mjp}$$

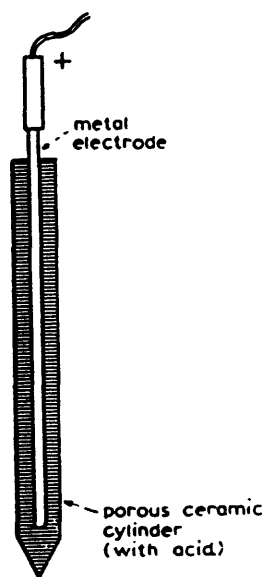
where m is the ionic mobility, τ is time, j is the current density, and ρ is the earth resistivity.

They indicate equation 2 applies very near the electrode where the electric field is nearly constant. For travel further from the electrode where the electric field can be considered as from point source they give:

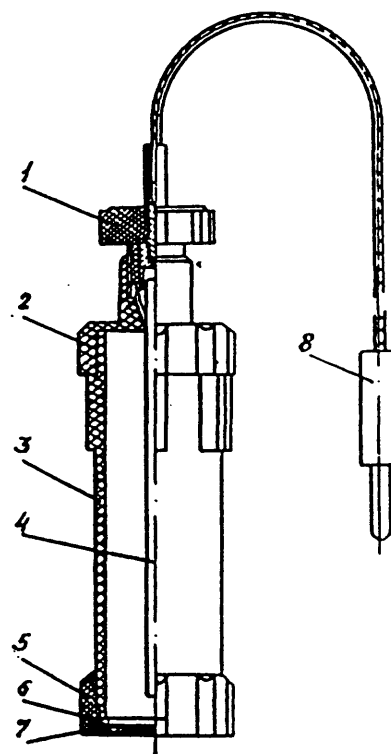
$$3. \quad \tau = \frac{4\pi}{3mi\rho} h^3$$

where i is the current.

Equation 3 applies to a point source in whole-space. For CHIM extractions that take



A.



B.

Рис. 11. Элементоприемник для наземных исследований:
1 - контакт, 2 - колпачок, 3 - цилиндр, 4 - электрод титановый, 5 - гайка, 6 - прокладка, 7 - мембрана, 8 - вилка однополюсная

- | | |
|-----------------------|-------------------------|
| 1. Contact | 5. Hose Cap |
| 2. Cap | 6. Washer |
| 3. Electrode body | 7. Parchment Membrane |
| 4. Titanium Electrode | 8. Electrical Connector |

Figure 3. Types of Russian CHIM electrodes or element receivers (EPR). A. A porous ceramic electrode several cm thick, from Shmakin (1985). B. Polyethylene electrode with parchment semi-permeable membrane, from Goldberg and others (1978). No dimensions are given, but fluid capacity is about 100 cm³.

place on the earth's surface the half-space formula is appropriate. This is just half the time given by equation 3. The implications of equation 3 of the volume sampled in a CHIM extraction do not appear to have been pursued, based on literature available to us. The relationships given in 2 and 3 are not even given in the extensive CHIM manual prepared by Rudgeofizika (in Bloomstein, 1990).

Based on equation 2 and 3 Ryss and Goldberg show idealized graphs, which they call hodographs, for the quantity of an ion collected as a function of time for a homogeneous earth (figure 4). In figure 4 this is the line ABMN, showing more rapid accumulation of ions on segment ABM, and reduced accumulation on segment MN. Goldberg and others (1978) attribute this flattening as being due to "the depletion of the particular ion in the treated volume of rock". This is in reference to extraction from a homogeneous rock mass. In a homogeneous earth, and for ideal CHIM extractions, such flattening of the accumulation-time curve can only occur if the anode is very close to the cathode, where counter ions from the anode have time to migrate to and enter the cathode.

Ryss and Goldberg's (1973) curves for an idealized simple two-layer model are also shown in figure 4, in which the lower layer, representing a mineralized zone, has an increased ion content. The deeper mineralized zone is reflected in the steeper accumulation curve indicated by the branch BC or DF which occurs at time t_{01} or t_{02} respectively. Ryss and Goldberg imply that t_{01} or t_{02} could be used to determine the depth to the mineralized layer. This paper also distinguishes two separate types of CHIM surveys, a primary or fundamental variation and an aureole version. In the aureole version the ions collected are only those present in a geochemical aureole above the deposit, presumably the action of the applied artificial electric field has not been long enough to bring ions directly from the deposit. Ryss and Goldberg (1973) provide no solid measure of the volume of soil that they would be sampling. The primary version is one in which they state the ions collected are derived directly from the ore zone. Such is the case for CHIM used in a borehole that penetrates ore. An example from a borehole study is given by Ryss and Goldberg (1973), and in Bloomstein (1990).

From an examination of the literature it appears the Russian researchers generally acknowledge that their surface field studies all represent measurements in the aureole version, although they hoped to accomplish the primary version from the surface as well. Ryss and Goldberg (1973) clearly believed that such was possible since they state "Investigation of the mobility of ions in various media showed that mobility varies from thousandths to thousands of $\text{cm}^2/\text{volt-hour}$ ". Electrochemical texts give simple ion mobilities in dilute solution generally in the range of 1.4 to 2.9 $\text{cm}^2/\text{volt-hour}$ with the fastest, H^+ , being 13 $\text{cm}^2/\text{volt-hour}$. From the above quotation it is clear that Ryss and Goldberg were talking about mobility of ions in solution moving under the action of an applied electric field, and were not referring to other forms of mass transport. The authors wonder if this belief in ultrafast mobilities played a role in Ryss and Goldberg's championing of the concept of the primary version of CHIM for deeply covered deposits, including those with transported cover.

This same year, 1973, S.G. Alekseyev in conjunction with Veikher and Goldberg

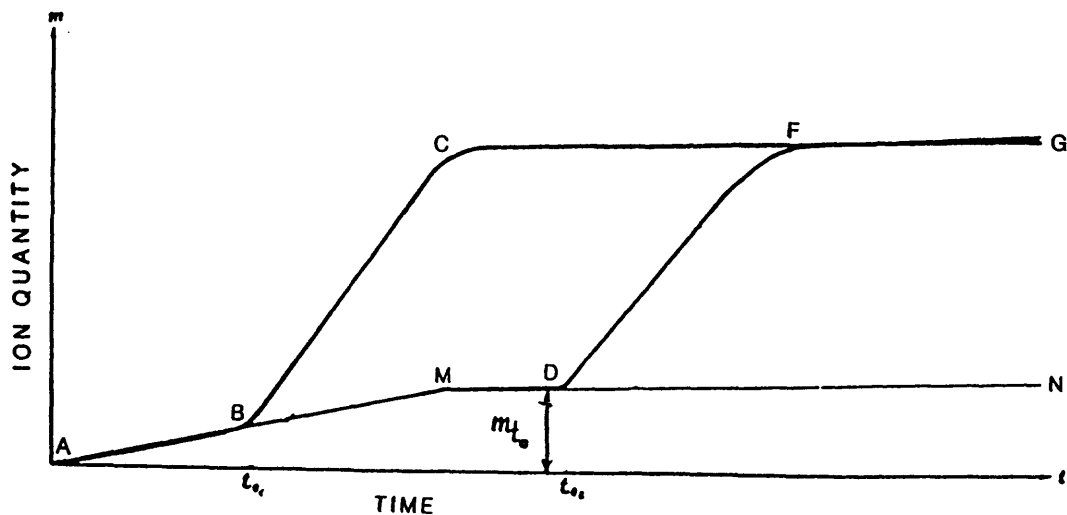


Рис.2. Схематические геоэлектрохимические годографы для двухслойного разреза при вступлении ионов в зону регистрации из второго слоя на начальную (AB) и на последующей (BD) ветвях годографа для первого слоя.

Caption Translation: *Schematic geoelectrochemical hodograph for a two-layered section showing the effect of ions coming out of the second (lower) layer on the initial (AB) and on the later branch (BD) of the hodograph for the first layer.*

Figure 4. Ryss and Goldberg's (1973) idealization of a CHIM curve showing ion accumulation as a function of time for a simple two layer model. The first layer curve is ABMN. Ions arriving at the surface electrode from the second layer are represented by the part BCFG for a shallow layer or by DFG for a layer of greater depth. Times T_{01} or T_{02} are used to determine the depth to the lower ion source.

published a paper titled "Possibilities of the CHIM method for exploration of covered gold deposits", and M.A. Alekseyeva and Ryss (1973) published the first part of an extended paper on ion movement in rocks due to an electrical current. From these papers it is clear that by this time the CHIM method was in the advanced stages of development in the USSR.

Throughout the rest of the 1970's and 1980's numerous papers were published by the VITR group working on CHIM. After 1980 the work was conducted in the all-Union Institute for Exploration Geophysics (VIRG) where Dr. Ryss was head of the Geoelectrochemistry and Geochemistry division. VIRG is part of NPO "Rudgeofizika". The technique was well enough advanced by 1978 that a technical manual was prepared instructing field crews in all the details of operation (Goldberg and others, 1978, and in Bloomstein, 1990). At the peak of its application in the USSR, there were 20 to 30 field crews in operation (A. Levitski, personal comm., 1994). Scintrex/Rudgeofizika (1990) note that 20 crews were in use in Russia in 1990. This large number of field crews must be an indication that the technique did provide useful information in exploration.

Because a CHIM extraction is, in principle, a simple Faradaic extraction of soil ions, it is puzzling to us that the Russian literature does not indicate the need to measure the charge delivered to each electrode. The detailed CHIM operations manual (Goldberg and others, 1978) makes clear that no attempt was made to deliver equal charge to every electrode. They state that "in the aureole version the controlling extraction parameters are the electric field intensity around the collection electrode, and the electric current". Further, they state that "the extraction processes are very complex and antagonistic, but that the electric field intensity is the most stable characteristic of the process". Based on empirical evidence they claim that the required electric field intensities and extraction times would be constant for any given region of exploration.

Accepted CHIM field procedure thus was to adjust individual electrode currents so that the electric field across two titanium electrodes placed into the soil, and spaced 20 and 30 cm from each collection electrode, were all equal. Whatever current was required at each electrode would then be held constant during a run. Clearly, by adjusting the local electric field, the charge delivered to each electrode was inversely proportional to the local site resistivity.

Most of the published CHIM studies available to us show results for base- and precious-metal exploration at the deposit scale. Besides these commodities, Russian literature states that CHIM methods were also used in exploration for Ni, Co, Mo, W, U, Sm, REE, Be, and oil and gas. An example of regional studies is given by Kirillov and others (1989) over the Dzhezkazgan geosyncline in which several sandstone hosted copper deposits occur. A 19 km-long profile adapted from Kirillov and others (1989) is shown in figure 5. This profile was made at a 20 m station spacing, using two 10-hour extraction cycles, with Rudgeofizika CHIM-10 equipment.

Details on the equipment and procedures used by the Rudgeofizika developers are given in Bloomstein (1990).

C. Diffusion Extraction Method

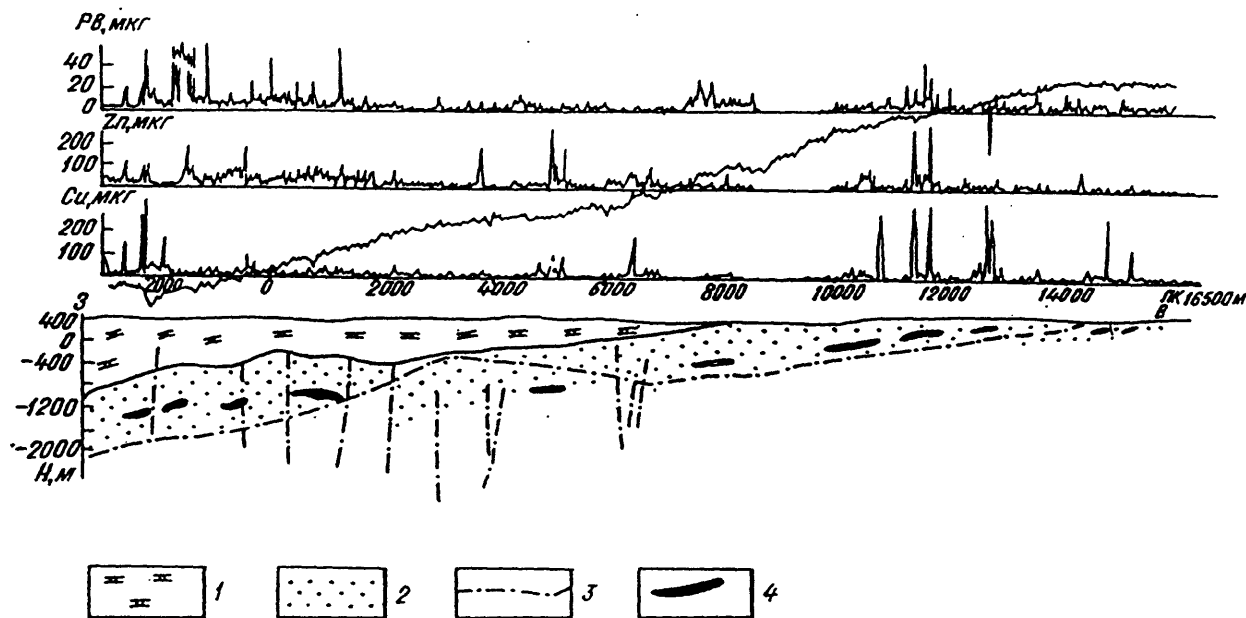


Figure 5. An example of a regional CHIM survey in the Dzhezkazgan region USSR, adapted from Kirillov and others (1989). Caption translation: *Results of observations with the CHIM method of a regional profile in the Dzhezkazgan geosyncline region. 1.-Slaty sandstone, siltstone, argillic kingite and fluid producing formation; 2.-Red and grey sandstone of the Dzhezkazgan formation; 3.-Tectonic fault mapped from results of seismic work; 4.-Deposits of copper sandstone, assumed from results of the CHIM method. Concentrations are in total micrograms. The meaning of the squiggly line passing diagonally across the Cu, Zn and Pb plots is unknown.*

An outgrowth of the Russian CHIM method, developed in the mid to late 1980's, is the method of diffusion extraction (MDI, metoda diffuzionnogo izvlecheniya); (Putikov, 1987; Alekseyev and others, 1989; Dukhanin, 1989). The Rudgeofizika researchers discovered that if the acid-filled EPR were emplaced in the soil as in a normal CHIM extraction, but no current applied, that they would obtain CHIM-like geochemical anomalies. They showed that diffusion processes were responsible for the collection of soil ions. This method has been evaluated over a number and variety of deposits (Dukhanin, 1989). To date, we have found no comparisons of MDI and CHIM results over the same deposit in the Russian literature.

Routine MDI extractions, however, were not done with the EPR, but generally used sausage casing filled with 150 cm³ of nitric acid and sealed. These “sausages” were then buried in the soil and left for about 24 hours after which time they were recovered, and the fluid was analyzed for collected metals.

Diffusion processes present significant problems in making CHIM extractions and the USGS has investigated these problems in some detail (Leinz and Hoover, 1993). We now believe that almost all past Russian CHIM results were essentially MDI extractions, and that the applied electrical current had very little effect.

D. The MPF and TMGM Methods of Extraction

MPF and TMGM are partial methods of extraction that, with CHIM, are discussed by Antropova and others (1992). Alekseev and others (1996) report MPF and TMGM as belonging to the category of geoelectrochemical methods of prospecting for deep mineralization that includes CHIM and MDI. MPF, a method for the selective extraction of organically bound forms of occurrence of elements, involves the extraction of metal-organic acid complexes (fulvic-humic complexes) from soils with a solution of sodium pyrophosphate. The extracts are analyzed for metals and carbon. Metal concentrations are normalized to carbon (M/C) to compensate for incomplete extraction of the organic material (Antropova and others, 1992). TMGM is described as a thermomagnetic method for the selective extraction of metals associated with secondary Fe and Mn oxides and hydroxides (Antropova and others, 1992; Alekseev and others, 1996). The extraction involves removal of primary magnetic minerals from the soil sample and firing the remaining sample under reducing conditions. The heat treatment reduces secondary iron-bearing minerals to strongly magnetic compounds which are removed by magnetic separation (Antropova and others, 1992). The magnetic separates are analyzed for metals either directly or following dissolution with acids.

MPF and TMGM are compared to CHIM in surveys conducted in Canada by Rudgeofizika in collaboration with Scintrex Ltd. in 1990 (Ryss and Seigel, 1992). Antropova and others (1992) provide no comparisons of the performance of the three methods at the same site. Alekseev and others (1996) compare results for MPF, CHIM and standard soil geochemistry extractions over the Semiletka Cu-Ni prospect, Kola peninsula, and MPF and CHIM extractions over the Montcalm site (Canada). No comparisons are given for MDI (referred to by Alekseev and others, 1996, as MDE) and CHIM extractions at the same site and the authors neglect to

give any results for TMGM.

II. Chinese Development of CHIM

In the early 1980's researchers in the Peoples Republic of China, PRC, began studies of the CHIM method (Liu, 1991), which they call "geochemical extraction" (Gao, date unknown), or "electro-extraction method" (Liu, date unknown). CHIM is considered one of a group of so called electrochemical methods which include partial extractions of organic or magnetic soil fractions, analogous to classifications used by Russian investigators. Gao (date unknown) breaks the CHIM technique down into five variants: 1. the halo, 2. deep seated extraction, 3. logging, 4. water extraction, and 5. charging extraction. The deep seated and logging variants correspond to the Russian's direct CHIM extraction. Water extraction refers to use of electrodes in water wells. It is not clear to us what Gao means by charging extraction.

Although our information on CHIM research in the PRC is limited by language problems, there are at least six centers at which such research has been conducted. One is at the Northeast Bureau of Geologic Exploration, in the Ministry of Nuclear Industry, at Shen Yang (Gao, date unknown), one at the Institute of Geophysical and Geochemical Exploration (IGGE), in the Ministry of Geology and Mineral Resources, Langfang, Hebei (Liu, 1991), one at the Nanjing School of Geology, Nanjing (Xu and others, 1989), another at the Guilin College of Geology, Guilin (Luo and others, 1993), one at the Beijing Institute of Mineral Resources of Geology (Ouyang Zongai, 1993, personal comm.) and the last at the Department of Applied Physics, China University of Geosciences, Beijing (Jinming and Jun, 1993).

A. Shen Yang Group

The Shen Yang group appears to follow closely the Russian technology, promoting CHIM for exploration of covered deposits that may be as much as 400 to 500 m deep. Gao (date unknown) in his paper gives examples of CHIM field surveys over both gold and uranium deposits. An example from the Ma Lan Yu gold placer shows a distinct Au anomaly over what is described as a recent deposit. Figure 6 shows results adapted from Gao (date unknown) over the Ma Lan Yu deposit. Gao also mentions that CHIM can be used for Pb, Zn, Cu, Ni, Co, and Mo exploration but gives no examples. He also clearly states that the method is based on the transport of deep seated ions into electrodes placed on the surface. However, there is no justification given for this statement. This may simply be repeating the Russian belief.

B. IGGE Group

The IGGE group appears to be the most active in CHIM research and the group with whom we have had the most communication. They state that CHIM may be used in exploration for Pb, Zn, Cu, Ni, Au, Ag, Sn, U, and oil and gas with an "effective detection depth of hundreds of meters" (Liu, 1991). When we first communicated with Liu Jimin of the IGGE in 1988, IGGE had modified the Russian version of the CHIM electrode to do away with the acid filled cathode. When base metals were the exploration target, they used a bare graphite rod as the

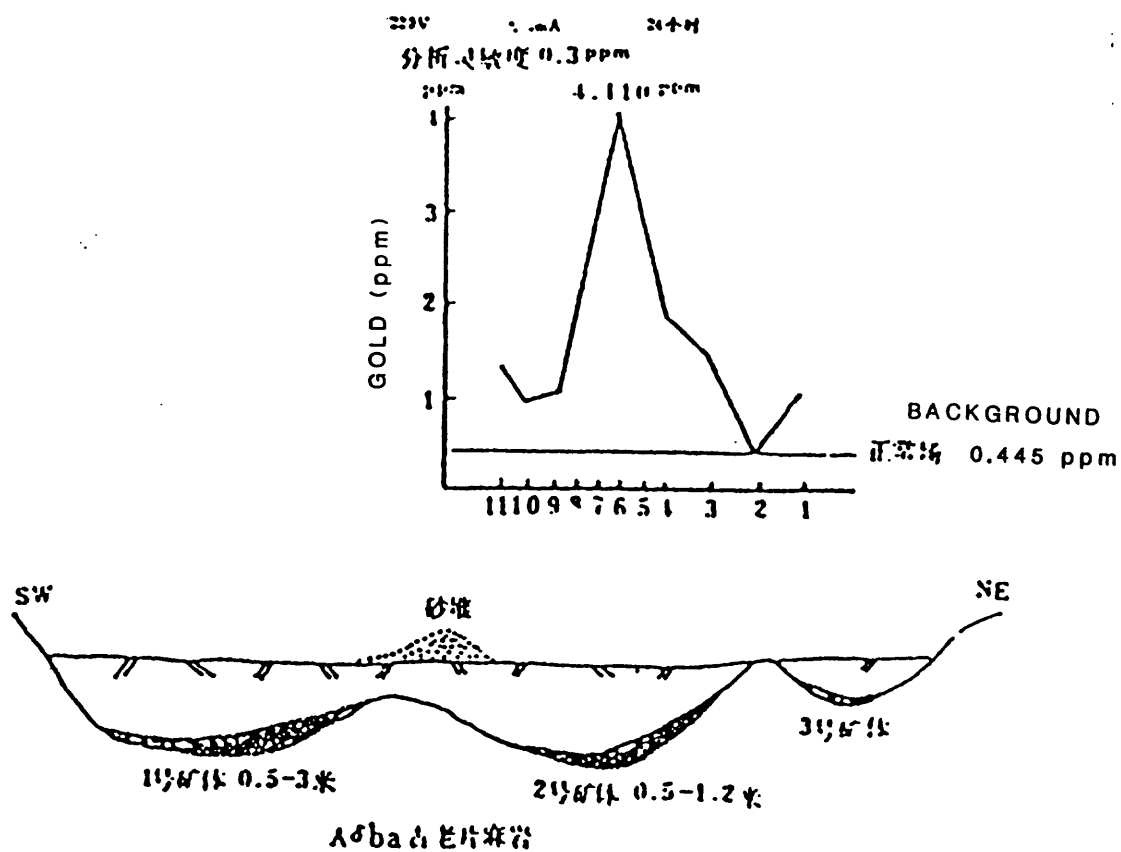


Figure 6. Geological section and CHIM results at the Ma Lan Yu placer gold deposit, China, adapted from Gao (date unknown). Station spacing is 5 and 10 meters.

collection electrode (cathode). The rod was buried in the soil, an unspecified amount of water was poured around the electrode, and the current turned on (150-300 mA at 220 volts for 20-34 hours). After the current was turned off, the graphite rod was retrieved and the surface was scraped to remove a thin layer of graphite. This graphite was then analyzed for the elements of interest. When gold was the exploration target, a polyurethane foam sleeve was placed around the graphite rod. Polyurethane selectively adsorbs gold ions as they migrate to the graphite. This assembly was buried in the soil, water added, and current applied. After the current was turned off, the assembly was retrieved and the foam sleeve was analyzed for gold.

Currently, the foam method is still used for gold exploration, but the technique for base metals has been modified. A new electrode has been developed which incorporates a powdered zeolite as an adsorption medium. A diagram of this electrode is shown in figure 7. The electrode is placed on the soil, about one liter of 1% nitric acid is applied to the soil, and current is applied (100-300 mA at 220 volts for about 24 hours). After application of the current, the zeolite is analyzed for the elements of interest.

Liu and others (1993) state that the group has conducted many tests beginning in 1985, including an extensive survey for gold covering 70 km². Their short paper presents CHIM results over three Au deposits, one Cu-Ni deposit, two Cu deposits, and mentions results over an oil field in Inner Mongolia. CHIM data for Cu, Ni, and Cr over the Cu-Ni deposit in Xinjiang which is at a 400 m depth define an anomaly directly over the deposit, exhibiting no evidence of lateral dispersion. Figure 8 shows their results. This paper by Liu and others (1993) is significant for discussing the first published data that we are aware of over an oil or gas deposit. Pb, Ni, Co, Mn and Cu in the organic fraction of soils over this 1 km deep oil field are shown normalized to carbon. However, they give no indication of how the carbon results were obtained. The data show haloes of Mn/C, Co/C, Ni/C Cu/C and Pb/C anomalies on the edges of the field. Sn/C is also stated to be anomalous at the edge of the field. They state that CHIM results were similar.

The IGGE group has also extended the technique to sampling well water for gold and silver. For this, the polyurethane-wrapped electrodes are used with a 6-v battery, and ion collection time extended to 19 days (Wu and others, 1989). Wu and others (1989) attribute the idea for this water extraction to Ryss and Goldberg.

C. Nanjing School of Geology

The Nanjing group produced the earliest published Chinese papers in our records (Fei, 1984; and Xu and others, 1984). Their initial work was done without knowledge of the Russian work (Xu and others, 1989), and used simple graphite electrodes. The first field testing with satisfactory results appears to have been done in 1984 over a copper deposit (Xu and others, 1989). The CHIM method has been used by this group to address the question of gold mobility in near-surface environments (Xu and others, 1989). The collection of gold through the CHIM process provides strong evidence for the presence of gold as an ionic species. With their graphite rods, and operating at 200 volts and 20 mA per electrode and running times of 60 and 96 hours, they found gold on the cathodes. Xu and others (1989) make the interesting comment "the

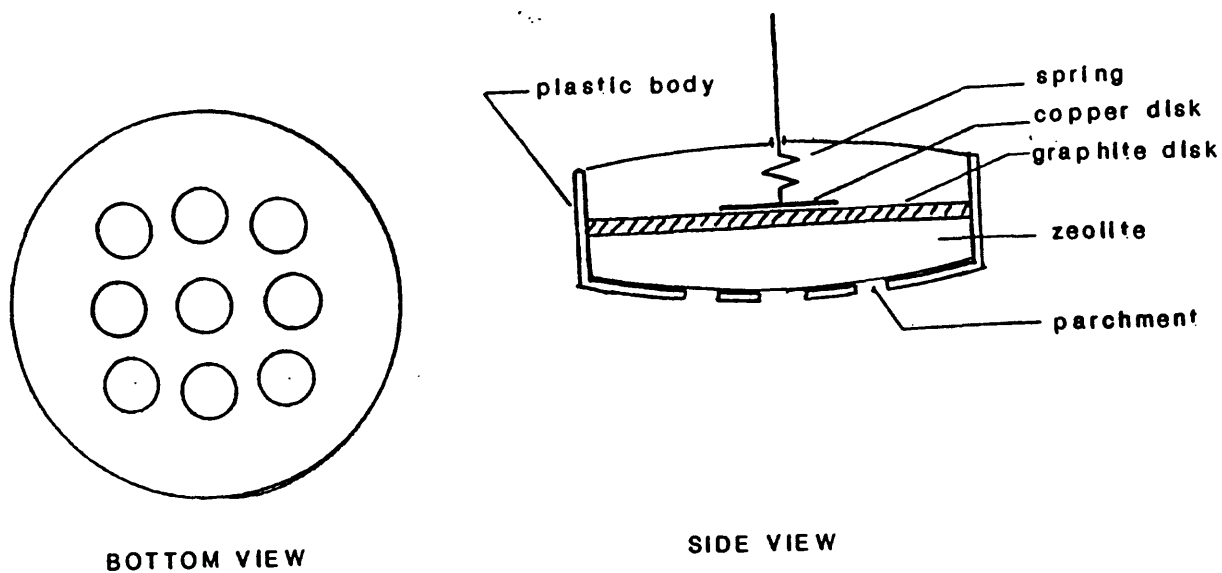


Figure 7. Sketch of an Institute of Geophysical and Geochemical Exploration (IGGE), China, electrode in which natural zeolites are used to collect ions.

35 线地电化学异常剖面图
Geo-electro-chemical Comprehensive profile for Line 35

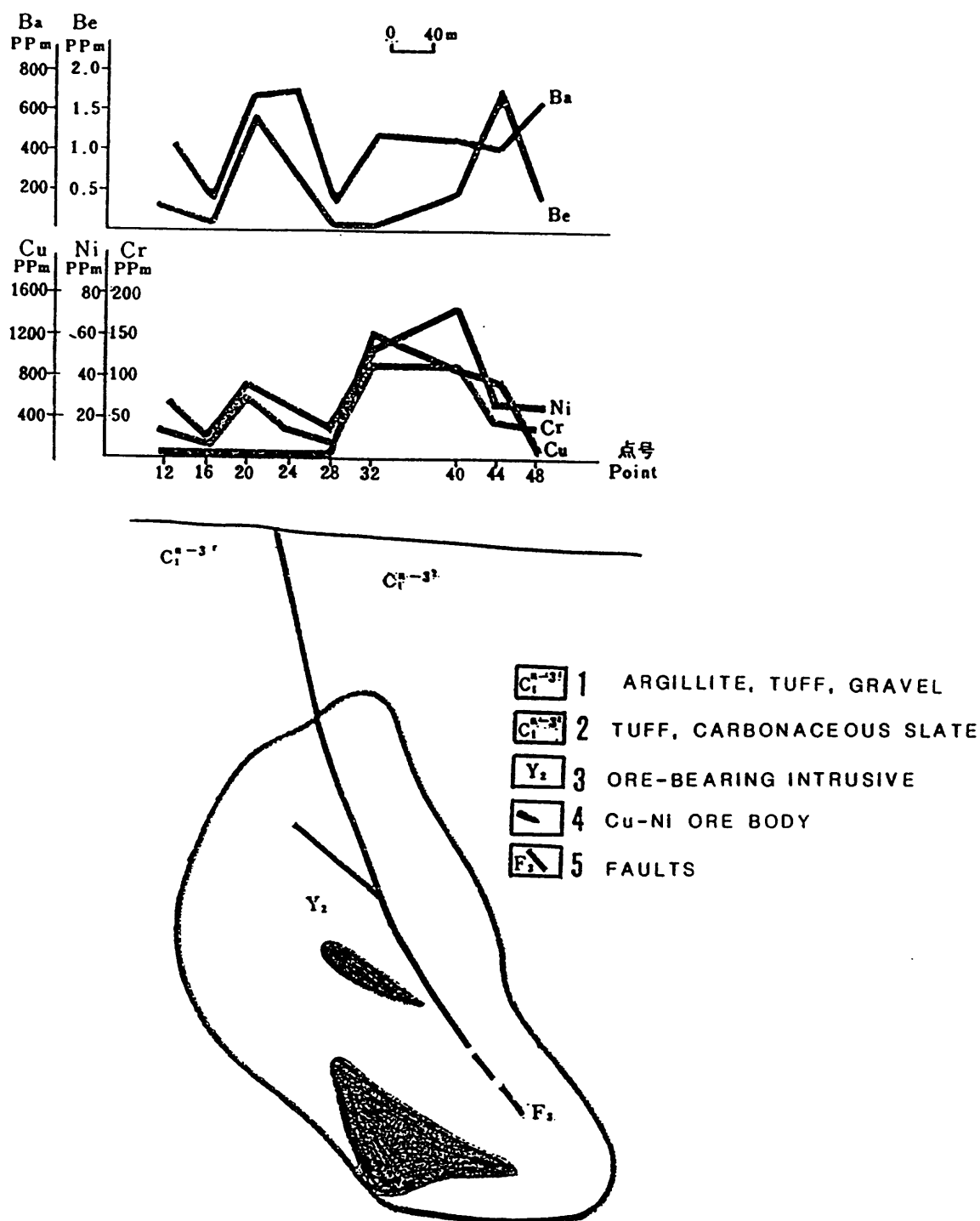


Figure 8. CHIM profiles and a geologic section across a Cu-Ni deposit, Xinjing, China, adapted from Liu and others (1993). Note that the Ni, Cr, and Cu anomalies are centered directly over the deposit.

amounts of Au extracted respectively by a strong current (500 mA) and a weak current (20 mA) for an equal time period at the Wuhe gold mine area in Anhui Province were not very different." The USGS has observed similar problems when using a more conventional Russian type system.

D. Beijing Institute of Mineral Resources and Geology

At Beijing, Ouyang Zongai, with the Beijing Institute of Mineral Resources and Geology has been conducting CHIM research. This research has looked at gold extractions over the Yang Shan deposit, Jiang Xi Province with comparable soil studies (Ouyang, personal comm., 1993). They have made studies along a single line, showing gold accumulation on CHIM collectors. They presumably used cation collectors, but of undefined type, with different power sources. These power sources were a 220 V generator source, 90 and 1.5 volt battery sources, and no applied voltage source. Gold anomalies above apparent background were seen on each run, but there was no replication evident in the data from the experiments with different power sources.

E. China University of Geosciences, Beijing

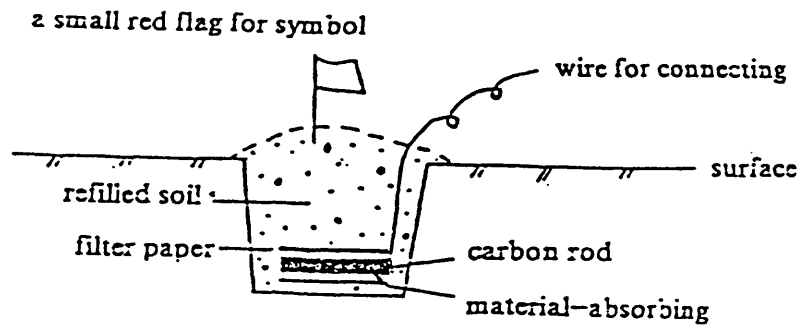
Jinming and Jun (1993) at the China University of Geosciences, Beijing, have also published results of their CHIM work. They developed an equation for the ion migration time in a half space that is equivalent to that presented by Ryss and Goldberg (1973) for a whole-space (equation 3). They also present experimental results for Cu^{2+} ion mobilities that are about twice the conventional value for dilute solution. In their paper, they point out the difficulty of moving ions for any distance in the earth during a CHIM extraction.

F. Guilin College of Geology

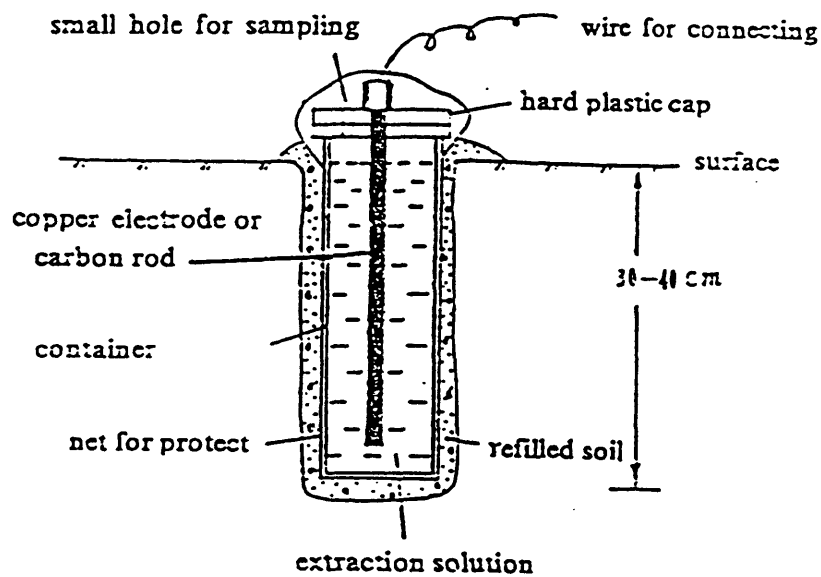
Luo and others (1993), with the Guilin College of Geology show comparisons between CHIM and soil extractions and compare CHIM results for different sampling times. This is one of very few papers that provide these comparisons, and such comparisons were the focus of some of the first USGS studies (Smith and others, 1993). Luo's group uses two "extraction methods": (1) a "deep extraction" using a 220 V a.c. source (applied d.c. potential not stated) with separate current control to individual fluid-filled electrodes; and (2) a "shallow extraction" with 1.5 V or 116. V battery sources, all the cathodes connected in parallel. Covered (Au absorbing material) graphite rods are used as collectors. They state that both the deep and shallow extraction methods are effective, but that the former gives greater depth and wider anomalies, while the latter gives higher intensity anomalies and better anomaly contrast.

Figure 9 shows sketches of Guilin College of Geology electrodes and how they are emplaced in the ground, adapted from Luo and others (1993).

Luo and others (1993) show soil geochemical data for Au before and after CHIM extractions at three different sites. These data indicate an increase in soil gold beneath the electrode after a CHIM run, and are used to show that ions do migrate to the electrodes. A comparison of Au extracted by use of the 1.5, 116, and 220 V



Sketch map of configuration of carbon rod with material-absorbing in site



Sketch map of configuration of an element receiver in site

Figure 9. Sketches of two types of CHIM electrodes used by the Guilin College of Geology, and the method of emplacement, adapted from Luo and others (1993). The fluid-filled container is assumed to be a porous ceramic cup because Luo and others state that it is easily broken.

systems is also given, but unfortunately extraction times are not. There is no correlation between the Au data except over a shallow (100 m deep) ore body where Au anomalies are of about the same magnitude. If the running time was about the same and the current roughly proportional to the applied voltage this provides yet another example that metal collection was not primarily by a simple ion mobility mechanism governed by Faraday's law.

Luo and others (1993) data for 5, 15, and 20 hour extractions show that the longer extraction times do not give 3 or 4 times the quantities of ions as would be expected in an ideal CHIM extraction for a homogeneous earth. Unfortunately important details of the experiment are not given. The USGS made similar observations in our early tests (Smith and others, 1993).

III. Geological Survey of India CHIM Development

At about the same time that the Chinese were developing their capability in the CHIM method, the Geological Survey of India (GSI) was also developing a capability (Banerjee and others, unpublished manuscript, Talapatra and others, 1986). Interest in the CHIM method by the GSI resulted from a visit to the USSR by R.C. Talukdar in 1980, who witnessed a CHIM-10 survey in Uzbekistan. On Talukdar's return to India the GSI designed field equipment similar to that used in the USSR, and conducted laboratory and field tests of the CHIM method in 1981. Initial tests were made at the Karnataka copper deposit (Talapatra and others, 1986). The initial tests were with a 6 channel system using cathode collection electrodes consisting of porous ceramic containers. Initial runs were at 165 mA constant current per electrode for 15 hours. Significant electrolyte loss ($4N\ HNO_3$) occurred with these electrodes, and the initial 300 ml of electrolyte was augmented periodically to make up for losses (Talapatra and others, 1986). On this test distinct anomalies in Zn, Cu, and Pb were observed directly over the ore zone which was at a depth of 60-70 m. The authors conclude that the technique would be useful in arid to semi-arid regions with transported cover where conventional geochemical methods have limitations. Bose (1987) notes that by 1987 the method was being used extensively in Rajasthan for Zn, Pb, Ni, Co, Cd, Cu and Ag exploration, and that several sets of instruments had been fabricated.

The GSI conducted laboratory tests of the method as part of their research program. This involved simple "sand box" experiments with a modeled deposit of crushed ore (Talapatra and others, 1986) and simple copper coulometer experiments to show that Faraday's law holds when a pulsating d.c. current rather than a steady current is used (Banerjee and others, unpublished). In the GSI work there were two departures from Russian technology that are important to note. One is a correction for fluid loss from the porous ceramic electrodes that were used. The loss was 10% to 50% of original electrolyte over a 6 hour period. Their electrodes normally held 300 ml of fluid. Because 2N to 4N nitric acid was used as an electrolyte, the soil beneath the electrode had a major input of acid. This clearly was a major problem that other practitioners didn't face, or didn't acknowledge. Veikher and others (1980) and Bloomstein (1990), however, do note that in Russian tests electrolyte was added periodically (every 5 hours) to their collection electrodes to compensate for evaporation. We find it strange that significant fluid loss could occur due to evaporation in such short time. The electrodes Veiker used had 40 cm² parchment membranes and were operated at 400 to 600 mA. More importantly, the GSI recognized that,

from Faraday's law, the ions collected should be proportional to the charge delivered to each electrode, and that the analytical results should be normalized to the charge used (Banerjee and others, unpublished). This rather obvious and fundamental correction is not mentioned in Russian or Chinese papers, and does not appear to have been used by either group.

The GSI approach evolved along more or less independent lines because they did not have access to translations of the Russian literature during the time that they were developing their system. Even as late as 1985 the only Russian paper available to the researchers was the paper in English by Shmakin (1985). Following the initial 6 channel CHIM system, the later systems developed by GSI contained 10 channels. Operations with this system were typically for 6-8 hours at currents of 200 mA per electrode. The GSI research effort appears to have slackened in recent years.

IV. Scintrex Ltd, Concord, Canada Tests

Although there was extensive development of CHIM in the USSR, and significant research effort in China and India, the 1980's saw very little effort on the part of Western mining companies or research groups to investigate the technology. The paper by Shmakin (1985) was the first in English to attract much attention to the new technology, and it was about this time that some western researchers began to take notice. One of the first to follow up on this was Scintrex Ltd. of Concord, Canada. Scintrex first became aware of the various "geoelectrochemical" methods, including CHIM, being practiced in Russia in 1983 (Ryss and Seigel, 1992). After prolonged discussions with the Ministry of Geology (USSR), a partnership was formed in 1991 between Scintrex and NPO Rudgeofizika. This new partnership is called "Geoelectrochemical Surveys Partnership (GECF), and has been introducing CHIM and several of the other Russian methods on a commercial basis to the West.

The first major western test of CHIM was by the GECF group in Canada in the Summer of 1990. This program was supported by the Canadian Ministry of External Affairs and International Trade, the Ontario Ministry of Northern Development and Mines, and 12 major mining companies, BHP Mines Ltd., BP Canada Limited, Cominco Ltd., Corona Corporation, Falconbridge Limited, Granges Exploration Limited, Hudson Bay Exploration and Development Co., Ltd., Inco Exploration and Technical Services, Inc., Lac Minerals, Ltd., Noranda Exploration Limited, Rio Algom Limited, and Teck Explorations Limited (Ryss and Seigel, 1992).

The Canadian tests were conducted under the direction of Dr. Ryss and involved a staff of 10 from Rudgeofizika. Field equipment was brought from Russia, and tests were run over a three-month period in Northern Ontario at five separate deposits. The deposits tested were the Montcalm Ni-Cu-Co deposit, the Chance site adjacent to the Kidd Creek volcanogenic massive sulfide (Zn-Pb-Ag) deposit, the Harker-Holloway Au deposit near Kirkland Lake, the Currie-Bowman polymetallic vein prospect and the Windjammer Au site on the Dester-Porcupine fault zone.

Ryss and Seigel (1992) show results of three types of the electrogeochemical surveys over the five deposits, CHIM, MPF (a soil organic extraction) and TMGM (thermomagnetic extraction method). In these tests, CHIM anomalies are seen directly over ore at all sites except for the Windjammer site, but there is not good correlation between element highs on MPF, TMGM, and CHIM profiles. Unfortunately no results are given on other types of soil partial extractions for these tests.

Ryss and Seigel (1992) note that an advantage of the CHIM method is that surface anomalies occur directly over mineralization. Goldberg (1990) also notes that anomalies have a column-like form over ore bodies, that the migration of ions over large distances is not fully understood, and suggests a "stream-line character" for ion migration. Goldberg appears to be referring to the restriction of CHIM anomalies to positions generally directly over deposits, with no broad dispersion noted in the surface expression. This very important area of research will not be directly addressed in this paper. However, the USGS research, although limited in areas of deep cover, generally supports other investigator's results that CHIM anomalies are very restricted. Goldberg (1990) also mentions that the CHIM method can locate ore deposits with overburden as great as 500-800 m including allochthonous cover of up to 200 m, and oil fields at 2-3 km depth. The Canadian tests used a 40 channel Russian system consisting of a 5-ton truck and 10kw power source, with electrodes covering 800 m of linear profile for each run. Although running time is typically 24-40 hours, 20 hours were normally used during the Canadian tests (Ryss and Seigel, 1992).

V. Scintrex Ltd, Australian Tests

Following the Canadian test program Scintrex/Rudgofizika presented symposia on Russian "electrogeochemical" methods in Australia in April, 1991. The symposia, Phase I of the Australian test program, were coordinated by the Australian Mineral Industries Research Association, Ltd. (AMIRA) at a cost of \$54,600 with 12 sponsors. Phase II of the project consisted of field testing over selected deposits similar to what was done in Canada. The field tests were completed in 1992, but results have not yet been released. At present Scintrex is not conducting further CHIM tests.

VI. Western Mining Company Interest

During the mid- to late 1980's several major western mining companies took an interest in the CHIM method, and we understand that some limited experiments were conducted. We are not aware of any published results from these studies.

Richard Van Blaricom, Chief Geophysicist of Cominco American Resources Inc., has been actively pursuing CHIM research from about 1990. He performs only cation extractions using a specially developed electrode employing an ion-exchange resin for cation collection similar to the method of IGGE in China. Van Blaricom calls the electrode, designed for surface and down hole applications, a "collectrode". He has reported results for three case histories over zinc, copper, and copper-nickel deposits (Van Blaricom, 1995). Van Blaricom has recently participated in a

group geochemical test program over two gold deposits at the Marigold Mine, Nevada. Results are expected to be reported in 1997.

VII. ExploTech Ltd, Ariel, Israel Studies

In 1993 ExploTech Ltd of Ariel, Israel began offering CHIM and MDI services to industry based on Rudgeofizika technology. Mr. A. Levitski, formerly with Rudgeofizika, is managing director of ExploTech. In field surveys conducted in Israel in 1994-1995 (Levitski, 1996) both anions and cations were extracted. Levitski appears to be the only other researcher outside the USGS to have developed the capability to extract both anions and cations. He also demonstrates the presence of oppositely charged cadmium species, showing Cd accumulation rate curves for both anode and cathode collectors.

VIII. USGS - Newmont Mining Begin Research

The USGS first became aware of the CHIM method during a visit to China by D.B. Smith and P.K. Theobald, Jr. in 1987. During a return visit in 1988, Smith and Theobald met with Liu Jimin of the Institute for Geophysical and Geochemical Exploration who directed the institute's CHIM effort. Liu and his colleagues reported many case histories where CHIM had been successfully used to define concealed ore bodies.

The first course of action by USGS researchers was to collect available Russian literature and to have selected papers translated (Bloomstein, 1990). Included in the translations was the complete technical manual on the CHIM method by Gold'berg and others (1978). With the knowledge of Chinese technology obtained by Smith and Theobald and using the Russian literature as a guide, the USGS embarked on a research program to develop understanding of the basic CHIM technology. It set out to determine the advantages and disadvantages of CHIM for assessment, exploration, and research applications. The USGS experience, major problems identified and some solutions are detailed in what follows.

Beginning in 1991 Newmont Mining joined the USGS in conducting field tests (Hoover and others, 1992a, 1992b, 1993). Results of early detailed field tests using conventional Russian technology at the Kokomo Mine, Colorado, have been reported by Smith and others (1993).

Problems identified in the early tests caused the USGS CHIM team to more closely examine the entire process. This resulted in discovery of the role that diffusion plays when acid electrolytes are used in the cathode (Leinz and Hoover, 1993). The discovery led to the development of an electrode of different design (Leinz and Hoover, 1994). With the new electrode, diffusion problems are minimized and Faradaic collection efficiencies improved by orders of magnitude. The new electrode, designated the NEOCHIM electrode, permits both anodic and cathodic extractions using neutral electrolytes of choice. Detailed testing has been conducted and comprehensive reports are in preparation.

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