Pilot study of partial extraction geochemistry for base metal exploration in a thick loess-covered region

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Abstract

The Jiaolongzhang polymetallic deposit in Eastern Gansu is located under loess terrains with thicknesses ranging from <50 m to >200 m. The mineralization zones are completely covered by loess and by a red soil layer. A soil survey along Line 48 by using the total digestion technique at a depth of 30 cm showed no responses for deposit-related elements Pb, Zn, Cu, and Ag. Different top soil leachants and leaching procedures were tested, and several elements were analyzed by using ICP-MS to decipher the leaching geochemistry in a loess terrain. Deionized water, NH4Cl, and HOAc did not detect any signals for the buried deposits, whereas 2% HCl leaching effectively detected buried deposits. Strong multi-point anomalies were found in many elements above the concealed ore bodies. The highest Cu, Pb, and Zn concentrations reached 800, 2000, and 8000 ng/g in the anomalous samples, respectively, and reached 200, 70, and 400 ng/g in the background samples, respectively. The elemental distribution patterns corresponded with the results of the metals-in-soil-gas survey. Most pH values of soil in background and anomalous samples were higher and lower than 8.45, respectively; thus, the pH values corresponded to a pattern of reduced chimneys.

Keywords:
Partial extraction
Geochemical exploration
Loess covered region

1. Introduction

One-third of the total land area of China is covered by transported regolith or sand, which negatively affects exploration geochemistry approaches that use surface samples. The plains in Eastern China are covered by thick alluvium, whereas the deserts in Northwestern China and the plateaus in Northern China are covered by loess. Despite the great potential for mineral exploration, some of these regions have been underexplored.

Loess covers c. 630,000 km² of the land area of Northern China, which encompasses the provinces of Xingjiang, Qinghai, Gansu, Shanxi, Shaanxi, Ningxia, Hebei, Inner Mongolia and Liaoning (Ren et al., 1995). The Jiaolongzhang polymetallic deposit in Eastern Gansu is the only mineral deposit in China that is located in a loess-covered area. Eastern Gansu also serves as a fine example of deep-penetrating geochemistry. The mineralization zones are completely covered by a half-solidified red soil layer and by loess with thicknesses ranging from <50 m to >200 m. A conventional soil survey that employed the total digestion technique at a depth of 30 cm showed no responses for deposit-related elements Pb, Zn, Cu, and Ag. In terms of metals in soil gas (MSG) or mobile nanoparticles, the soil survey showed that Cu, Pb, and Bi exhibited strong anomalies above buried ore bodies (Wang et al., 2008).

New models that account for the development of weak dispersion halos in transported covers (Cameron and Leybourne, 2005; Cameron et al., 2002, 2004 and Hamilton, 1998; Mann et al., 1998) indicate that metals migrate upwards in different forms and develop geochemical anomalies in the top soil. However, the mechanisms for such dispersion are still being debated. Soil covers hinder surface mineral exploration because these terrains do not have any outcrops. However, soil covers can preserve the geochemical signals from concealed or blind deposits. Several approaches, such as MMI, enzyme leaching, MOMEO leaching, electrochemical extraction (CHIM), MSG (geogas), have been devised to discover weak geochemical halos in soil and soil gas from concealed metal mineralizations (Bajc, 1998; Clark, 1993; Hall, 1998; Kang, 2009; Luo, 2004; Mann et al., 1998; Sun et al., 2011; Wang, 1998; Wang et al., 2008). MSG (geogas) detects low concentrations of elements from concealed deposits of soil gasses or nano-particles. Partial extraction techniques, such as MMI, enzyme leaching, and CHIM, physically separate low concentrations of trace elements that are loosely attached to the soil related to the concealed mineralization by these secondary mechanisms from the trace element contents inherited from the transported regolith itself. MMI has been successfully commercialized, and hundreds of researchers have adopted MMI in cases studies.

MSG and CHIM have been investigated by several case studies in China (Gao et al., 2011; Kang, 2009; Luo, 2004; Sun et al., 2011; Wang et al., 2008). However, no significant advances have been achieved in the application of partial extraction for mineral exploration in
transported overburdens without metal anomalies. Few studies have also investigated the extraction of specific element species, such as water soluble, adsorbed, exchangeable, bound to carbonate, bound to organic matter, bound to Mn oxides, and bound-to-amorphous Fe oxides in strategically low densities (Wang, 1998; Wang and Xie, 1996; Wang et al., 1997, 2007 and 2011). While MSG surveys have relatively poor reproducibility and are difficult to use at the reconnaissance stage because of their sensitivity to several factors, such as climate, cover features, and personal operations. Therefore, an effective partial extraction method must be devised and the distribution of elements above sulfide deposits in China must be investigated to promote the application of geochemicals in mineral exploration in overburdens. This paper proposes a partial extraction method that can locate buried deposits in loess-covered terrains without total anomalies.

2. Geological setting

The study area is a typical loess landform with a semi-arid climate. The groundwater table lies at the bottom of the loess. The study area has a 420 mm average annual precipitation and 730 mm evaporation. The groundwater table lies at the bottom of the loess. The study area deposits in loess-covered terrains without total anomalies.

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2. Geological setting

The study area is a typical loess landform with a semi-arid climate. The groundwater table lies at the bottom of the loess. The study area has a 420 mm average annual precipitation and 730 mm evaporation. The study area is also rich in alkaline with different pH levels (9 to 9.7 in water, 8.4 to 9 in top loess, 8.6 to 9.5 in deep loess, and 9 to 9.7 in red soil layer).

Over 90% of the area is covered by fine-grain loess (less than 0.076 mm in diameter) and mainly comprises quartz, calcite, feldspar, and clay (kaolinite, illite, and montmorillonite) minerals (Table 1). Approximately half of the minerals in the top and deep loess are clay, and over 10% of these minerals are calcite.

The Jiaolongzhang VMS deposit was discovered in 1974 via an aeromagnetic survey (Wang et al., 1979). The polymetallic mineralization zones are c. 3600 m in length, 200 m in width, and 300 m to 500 m in depth. These zones are completely covered by loess (50 m to 80 m in depth) and by a half-solidified red soil layer (20 m to 50 m in depth) that is deposited as lake sediment below the loess (Fig. 1). The overburden is geochemically homogeneous and has minor concentration variability for most elements (Wang et al., 2008).

Buried ore bodies mainly comprise Cu, Pb–Zn, and pyrite. The bed rock is mostly composed of intermediate and acidic marine volcanics, pyroclastics, and felsic sandstone, which are only exposed at the bottom of the gullies. The intrusive rocks in this area are mostly granodiorite and plagiogranite porphyry, the host rocks are chlorite-quartz sandstone and limestone, and the main supplied minerals are pyrite, sphalerite, galena, and chalcopyrite.

3. Method

3.1. Sampling

A total of 15 samples along Line 48 coordinating with geological exploration profile were taken from the farmland. These samples were extracted from 30 cm below the lower interface to ensure that these elements were free from human contamination. Results from MSG survey in the same sites finished by Wang et al. (2008) were also used to compare with the selective leaching results of the present study. Over 250 g of air-dried soil were sieved to −200 meshes in the laboratory for further analysis.

3.2. Analysis

3.2.1. Total

The total trace element concentrations were determined by the central Lab of Geophysical and Geochemical Exploration using Thermo fisher X 2 ICP–MS after digesting the soil samples in a hot four-acid mixture.

3.2.2. pH

pH was measured by pocket pH following 10:1 deionized water/soil leaching.

3.2.3. Sequential partial extraction

Given the mineral composition of loess, the majority of mobile metals in loess soil were assumed to be water extractable, adsorbed, exchangeable, and bound to carbonate. Therefore, the three sequential leaching stages frequently used by Chinese researchers were employed in this study to test if the proposed procedures could detect the anomalies derived from buried minerals.

A 5 g soil sample was placed in a 200 ml plastic bottle and was sequentially leached by different extractors, such as water, NH₄Cl, and HOAc. Fig. 2 shows the sequential leaching scheme, which involves the following stages:

**Water-extractable metals**

1. A 5 g sample was placed in a 200 ml polypropylene bottle. The sample was then mixed with 50 ml 18 Ω Mini-Q water.
2. The mixture was shaken and left overnight.
3. The liquid was centrifuged and filtered through a 0.45 mm Millipore filter into another 100 ml polypropylene bottle.
4. The liquid leachate was immediately stabilized with 1 ml ultrapure nitric acid for multiple element analysis.

**Adsorbed and exchangeable metals**

5. 50 ml NH₄Cl concentrations were added to the residue produced from step 3. Steps 2 to 4 were repeated.

**Bound to carbonate metals**

6. 50 ml HOAc concentrations were added to the residue produced from step 5. Steps 2 to 4 were repeated.

The leachate from steps 4, 5, and 6 were analyzed for Cu, Pb, Zn, Co, Ni, Mo, Sb, and Mn by using Thermo fisher ELEMENT 2 ICP–MS in the IGGE central laboratory.

3.2.4. HCl leaching

Low concentration HCl was used to extract weak bound metals from the soil by following steps 1 to 4. HR–ICP–MS was used to analyze the leachate for Cu, Pb, Zn, Ag, Bi, Cd, Ni, Co, Cr, Sb, Mn, Zr, Cs, Mo, and Nb.

4. Results

4.1. Blank

The reagent blank must be kept low in the metals to obtain reliable selective leaching data.

Cu and Pb had low blanks in most reagents (<1 ng/ml), except in 2% NH₄Cl (≥1 ng/ml) (Table 2). Zn had blanks higher than 1 ng/ml in all reagents. The blanks of Sb in deionized water, HOAc, and HCl were

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>Calcite</th>
<th>Kaolinite</th>
<th>Illite</th>
<th>Montmorillonite</th>
<th>Others</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jsp-2-7</td>
<td>29.00</td>
<td>9.62</td>
<td>12.58</td>
<td>10.30</td>
<td>16.70</td>
<td>19.58</td>
<td>3.82</td>
<td>Top loess</td>
</tr>
<tr>
<td>Jsp-2-6</td>
<td>33.38</td>
<td>8.83</td>
<td>11.36</td>
<td>6.7</td>
<td>16.15</td>
<td>18.67</td>
<td>4.63</td>
<td>Deep loess</td>
</tr>
</tbody>
</table>

less than 0.1 ng/ml but were higher than 0.1 ng/ml in NH4Cl. The blank of Bi in all reagents was considerably low (<0.06 ng/ml). All reagents in different concentration were low and consistent in metals and good for partial extraction.

4.2 Total digest

Fig. 3 shows the distribution of the total Cu, Pb, Zn, and Bi along Line 48. The total of the deposit elements are homogeneous in the soil. Samples 10 and 11 slightly decrease above the buried ore bodies. Therefore, the use of conventional soil survey as an exploration tool would pose significant challenges.

4.3 Sequential extraction

4.3.1 Water-extractable metals

Water-extractable elements Cu, Pb, and Zn related to mineralizations in the loess were few and exhibited high variations along Line 48 (Fig. 4). Although Pb and Zn slightly increased above the ore bodies, the response ratio was small.

Fig. 5 shows the water leaching results at different periods. The amount of water-leached metals did not increase unanimously with time even though the distribution patterns of the elements that were leached at different periods were similar. Therefore, water leaching should last for a short period only.

4.3.2 Adsorbed and exchangeable metals

Fig. 6 shows the distribution of Cu, Pb and Zn that were leached by 05%, 1%, and 2% NH4Cl. The Cu, Pb, and Zn that were leached by different

Table 2

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.44</td>
<td>0.37</td>
<td>1.557</td>
<td>0.008</td>
</tr>
<tr>
<td>0.5% NH4Cl</td>
<td>0.736</td>
<td>0.586</td>
<td>2.235</td>
<td>0.01</td>
</tr>
<tr>
<td>1% NH4Cl</td>
<td>0.937</td>
<td>0.807</td>
<td>2.168</td>
<td>0.01</td>
</tr>
<tr>
<td>2% NH4Cl</td>
<td>1.683</td>
<td>1.335</td>
<td>3.524</td>
<td>0.03</td>
</tr>
<tr>
<td>1% HOAc</td>
<td>0.64</td>
<td>0.34</td>
<td>2.041</td>
<td>0.038</td>
</tr>
<tr>
<td>2% HOAc</td>
<td>0.44</td>
<td>0.34</td>
<td>2.873</td>
<td>0.051</td>
</tr>
<tr>
<td>4% HOAc</td>
<td>0.42</td>
<td>0.39</td>
<td>2.938</td>
<td>0.054</td>
</tr>
<tr>
<td>0.5% HCl</td>
<td>0.507</td>
<td>0.402</td>
<td>2.161</td>
<td>0.005</td>
</tr>
<tr>
<td>1% HCl</td>
<td>0.568</td>
<td>0.343</td>
<td>2.408</td>
<td>0.008</td>
</tr>
<tr>
<td>2% HCl</td>
<td>0.832</td>
<td>0.601</td>
<td>5.798</td>
<td>0.011</td>
</tr>
</tbody>
</table>
concentrations of NH₄Cl did not exhibit any responses above the buried ore bodies. The distribution patterns of these elements were dissimilar because they were de-adsorbed and adsorbed into the liquid–soil system at the same time. Therefore, although half of the loess in the study area comprised clay minerals, the adsorbed and exchangeable metals were not the major elements in the loess soil.

4.3.3. Bound to carbonate metals

Cu, Pb, and Zn increased with increasing concentrations of HOAc. The highest percentages of these elements (up to 200 ng/ml) were leached by 4% HOAc (Fig. 7). The Zn that was leached by 2% and 4% HOAc exhibited weak anomalies, and the Cu and Pb bound to carbonate showed no responses above the ore bodies.

4.4. HCl leaching

Unlike in the MSG survey, the water-, NH₄Cl-, and HOAc-leached soil in Line 48 did not exhibit marked responses in this study. Therefore, the transportation of metals from the deeply buried ore bodies to the

![Fig. 3. Distribution of the total Pb, Zn, Cu, and Bi along Line 48.](image)

![Fig. 4. Distribution of water-extractable elements Pb, Zn, and Cu along Line 48.](image)

![Fig. 5. Water leaching results at different time periods.](image)
surface were not in the form of specific geochemical phases, such as free ions, absorbed, exchangeable, and bound to carbonate. HCl was used to extract all metals that were weakly or loosely attached on the exterior of the surface soil particles.

4.4.1. 0.5% HCl leaching

The 0.5% HCl-leached small metals (Fig. 8). Cu and Bi demonstrated small changes along Line 48, whereas Pb and Zn demonstrated significant changes but did not show marked anomalies with a favorable signal-to-noise ratio over the buried ore bodies.

4.4.2. 1% HCl leaching

When compared with the 0.5% HCl leaching, the Pb and Bi that were leached by 1% HCl did not increase, whereas the Cu and Zn showed a slight increase (Fig. 9). Cu and Pb were consistent along the entire line, whereas Zn and Bi showed one weak anomaly over a noisy background above the buried ore bodies, which indicated that higher HCl leaching might yield better results.

4.4.3. 2% HCl-leaching

The metals leached by 2% HCl significantly increased compared with the data by 0.5% and 1% HCl leaching. The leached Cu, Pb, Zn, and Bi over mineralized zone showed greater variations in comparison with that in background area and reached as high as c. 1026, c. 1879, c. 3360, and c. 0.47 ng/g, respectively (Table 3). Cu, Pb, Zn, and Bi exhibited strong responses over the mineralization (Fig. 10), thus implying that partial extraction could be used as a geochemical tool for mineral exploration in loess-covered areas.

4.4.4. 3% HCl-leaching

The metals leached by 3% HCl significantly increased compared with the data by 2% HCl leaching, particularly in the background area (Fig. 11). However, Cu and Bi leached by 3% HCl did not show marked anomalies over the buried ore bodies and the signal to noise ratio of Pb and Zn related to mineralization are much lower than that by 2% HCl leaching. It can be concluded that the natural minerals of the soil or specific soil substrates were significantly attacked by 3% leaching and it is essential that orientation studies should be done to select appropriate leachants and their concentrations on the base of the soil features in different landscapes for better use of partial extraction.

5. Discussions

5.1. Quality control (QC)

It is important to maintain a check sample program to get reliable results for deep-penetrating geochemistry. The total of elements in the soil was determined by commercialized IGECE lab with sophistically QC system. However, there was no standard reference material for
specific partial extraction now, so two duplicate samples should be inserted within each extraction of 15 samples to monitor precision.

The results for duplicate pairs for laboratory repeat samples for selected elements are presented in Table 4. The relative errors between pairs are less than 10%, which indicates that the analytical results of 2% HCl leaching are reliable.

The same conclusion can be made from the results of 2% HCl leaching by different person in different time (Fig. 12 and Fig. 13). Fig. 12 shows that the results by Wu (Wu, 2009) (data source of this paper) are positively correlated with Liao, 2011 (Liao, 2011) as a whole although Cu, Pb and Bi by Wu, 2009 seem systematically higher than that by Liao, 2011 and only Zn is slightly lower than Liao, 2011 in background samples. The difference between pairs (PD) of Cu from 15 samples is less 10%, the PD of Zn and Bi are less than 30% and only some PD of Pb are slightly higher than 30% (Fig. 12). Therefore the authors think analytical reproducibility of 2% HCl extraction is good and the developed partial extraction can be used as a powerful surface geochemical tool for mineral exploration in loess cover regions.

5.2. Partial extraction versus the MSG survey and pH

To understand the effectiveness of 2% HCl-leaching procedure, the results of the previous MSG survey by Wang et. al. (2008) were plotted on the same figure with the data by 2% HCl-leaching just for comparison (Fig. 14). The distribution of 2% HCl-leached Cu, Pb, Zn, and Bi along Line 48 coincided with that shown in the MSG survey, which indicated that anomalous metals from deeply buried deposits could be loosely

<table>
<thead>
<tr>
<th>Table 3</th>
<th>The results of 2% HCl leaching in line 48 (ng/g).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Background area (n = 9)</td>
</tr>
<tr>
<td></td>
<td>Min</td>
</tr>
<tr>
<td>Cu</td>
<td>289</td>
</tr>
<tr>
<td>Pb</td>
<td>40.9</td>
</tr>
<tr>
<td>Zn</td>
<td>541</td>
</tr>
<tr>
<td>Bi</td>
<td>0.01</td>
</tr>
</tbody>
</table>
attached on the exterior of the surface soil particles or in soil gasses in a
semiarid loess-covered area. Selective leaching had a high potential for
locating concealed minerals in similar landscapes considering its ease of
use and repeatable anomalies in comparison with the MSG survey.

Fig. 14 also shows the distribution of Pb, Zn, Cu, and Bi by 2% HCl and
pH by deionized water in soil along Line 48. Most pH values of soil in the
background samples were higher than 8.40, whereas the pH values of
soil in the anomalous samples above the buried ore bodies were lower
than 8.40, which reflected a pattern of reduced chimneys (Hamilton,
1998). Therefore, reduced chimneys over sulfide deposits could also
exist in an alkaline environment.

5.3. The data interpretation

In exploration geochemistry, selective leaches are used to dissolve
minerals that may include a high proportion of the mobile phase of
elements, including material derived from deposits (Cameron et al., 2004).
Soil-forming processes convert primary minerals derived from rocks into minerals stable at low temperature. The element
fraction that comes from primary minerals is here considered as the
internal or endogenic phase. Elements from external sources, including
a mineral deposit, are termed the exogenic phase. The exogenic phase is
initially added to the soil in water-soluble form or nano-particles. Each
secondary mineral contains elements of both endogenic and exogenic
origins. The principal aim of the selective leaches is to remove the
smallest amount of metal ions, nano-particles or other exogenic
minerals from soil while leaving the endogenic substrate unaffected.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample</th>
<th>Duplicate</th>
<th>RE(%)</th>
<th>Sample</th>
<th>Duplicate</th>
<th>RE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>411</td>
<td>353</td>
<td>3.80</td>
<td>373</td>
<td>269</td>
<td>8.10</td>
</tr>
<tr>
<td>Pb</td>
<td>129</td>
<td>88</td>
<td>9.45</td>
<td>211</td>
<td>250</td>
<td>4.23</td>
</tr>
<tr>
<td>Zn</td>
<td>738</td>
<td>702</td>
<td>1.25</td>
<td>1537</td>
<td>1347</td>
<td>3.29</td>
</tr>
<tr>
<td>Bi</td>
<td>0.04</td>
<td>0.05</td>
<td>5.56</td>
<td>0.13</td>
<td>0.11</td>
<td>4.17</td>
</tr>
</tbody>
</table>

Fig. 10. Distribution of 2% HCl-leached Pb, Zn, Cu, and Bi along Line 48.

Fig. 11. Distribution of 3% HCl-leached Pb, Zn, Cu, and Bi along Line 48.
In the loess covered terrain the traditional procedures to extract specific forms of metals in soil including ion, exchangeable and bound to carbonate did not succeed in finding metal anomalies over the known VMS mineralization. The HCl is a stronger leachant and could dissolve several forms of soil including ion, nano particles, exchangeable and bound to carbonate, bound to Mn oxides, bound-to-amorphous Fe oxides and even clay minerals with different concentration. The soil in study area is rich in carbonate and clay (Table 1). Like proprietary leach MMI the 2% HCl leaching is likely to extract several forms including ion, nano particles, exchangeable and exogenic carbonate and get good response to deeply buried VMS deposit. However with increasing concentration of HCl more carbonate and some part of bound to Fe–Mn oxides and even clay minerals might be dissolved, the concentration level of extracted metals rose sharply but the signal to noise ratio related to mineralization fell down significantly. Therefore the signals related to concealed ore bodies might be presented in particular forms and to better use partial extraction orientation studies should be done to select appropriate leachants and their concentrations on the base of the soil features in different terrains.

6. Conclusion

The results from the selective leaching of soil in Line 48 by water, NH₄Cl, and HOAc indicated that the metals transported from deeply buried ore bodies to the surface were not in a single geochemical phase, such as free ions, absorbed, exchangeable, and bound to carbonate.

The 2% HCl leaching of soil is likely to extract several forms including ion, nano particles, exchangeable and bound to carbonate from the soil (only one particular form with signal related to the mineralization) and provided strong responses for the deeply buried minerals. However, the procedure that is useful for the study area may not be useful for other landscapes. Therefore, future studies must examine the usefulness of selective leaching in other terrains.

A low pH level and a high amount of Zn, Cu, and Pb in soil above the sulfide ore bodies confirmed the existence of a reduced chimney in an alkaline environment.

The distribution of 2% HCl-leached Cu, Pb, Zn and Bi coincided with that of the MSG survey. Anomalous metals from deeply buried deposits...
were loosely attached on the exterior of the surface soil particles or in the 'gaseous' forms suspended on soil atmosphere in a semiarid loess-covered area. Partial extraction and MSG survey can be used as deeply penetration geochemistry in overburden, but the selective leaching is easier to be operated both in sampling and analyzing and has better analytical reproducibility.

Several case studies of the MSG (geogas) survey on concealed mineralization confirmed that deep-penetrating geochemistry, including MSG and selective geochemical extractions, was not the "silver bullet" for areas with thick transported or deeply weathered covers because barren and ore-bearing pyritic conductors could not be easily differentiated when used in grassroots exploration.

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**Fig. 14.** Distribution of the 2% HCl leaching and soil pH versus the results of the MSG survey along Line 48.
vice chairman of the Centre Lab at IGGE for their assistance in sample analysis.

References


