Differentiation of copper, molybdenum and tungsten in local biogeochemical cycles

V. Ermakov1, V. Danilova1, S. Khushvakhtova1, A. Degtyarev1, E. Krechetova1, S. Tyutikov1;
A. Buryak2, I. Pytsky2, B. Khabarov2
1V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry of RAS, Moscow
2A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Moscow

ermakov@geokhi.ru; akburyak@ipc.rssi.ru

A comparative assessment of biogenic migration of Mo, Cu and W in different molybdenum-tungsten-copper deposits and background areas has carried out.

Key words: biogeochemistry, cycles, copper, molybdenum, tungsten, habitat, organisms

Citation: Ermakov V. V., V. Danilova, S. Khushvakhtova, A. Degtyarev, E. Krechetova, S. Tyutikov; A. Buryak, I. Pytsky, B. Khabarov (2012), Differentiation of copper, molybdenum and tungsten in local biogeochemical cycles, Vestn. Otd. nauk Zemle, 4, NZ9001, doi:10.2205/2012NZ_ASEMPG.

Introduction

We have determined some trace elements content levels in soils, aquatic plants and/or animals (namely, in cattle blood & hair samples) in the conditions of some open cast deposits or background territories of the North Caucasus and Transbaikalia [Ermakov, Soboleeva, 2008; Ermakov et al., 2011]. The purpose of this study was to clarify the characteristics of accumulation of copper and molybdenum in animals on a background of different content of tungsten in the environment and feed and the possible inclusion of tungsten in the xanthine-oxidase of milk cows.

Methods

The field studies were conducted in summer, 2011 in the mining landscapes of tungsten & molybdenum deposits of Tyrnyauz, and in background areas of the North Caucasus through rocks, soil, waters, plants and/or animal sample selection. Determination of copper or molybdenum levels in most of the samples was measured by atomic absorption method using standard processes. The content of tungsten was determined by means of ICP-mass-spectrometry. The technique accuracy levels were checked using soil, plants or hair standard samples.

Results

It was established the enrichment the enrichment of soil-forming rocks by trace elements (Cu, Mo, W) in the Tyrnyauz area. The content of this elements here is higher the order, than in rocks of Chegem valley (background area). In water of Boksan-river and its inflows Zn concentration 1.5–7 times higher in comparison with Chegem-river waters. On some river-sites Mo, Pb, Ni and As concentrations are increased. It was discovered that soils of Baksan-river valley are significantly enriched with Mo и W (the enrichment coefficient (EC) 44–85 and 35–100, respectively), that is connected with displays of corresponding ore mineralization (Table 1).

Table 1. Parameters of biogenic migration of Mo and Cu in biogeochemical food chain

<table>
<thead>
<tr>
<th>Object</th>
<th>Mo, mg/kg</th>
<th>Cu, mg/kg</th>
<th>EC</th>
<th>Kb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anomal areas (Upper Mukulan, Tyrnyauz, Bilim)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water (8)</td>
<td>0.002–0.40</td>
<td>0.0027–0.076</td>
<td>5–400 (Mo) &lt;br&gt; 2.2–2.7 (Cu)</td>
<td></td>
</tr>
<tr>
<td>Soil, dump (8)</td>
<td>87–443</td>
<td>25.2–60.8</td>
<td>44–85 (Mo) &lt;br&gt; 1.9–2.4 (Cu)</td>
<td></td>
</tr>
<tr>
<td>Hay crop of plants (8)</td>
<td>7.2–64.5</td>
<td>3.0–10.6</td>
<td>14–20 (Mo) &lt;br&gt; 0.08–0.29 (Mo) &lt;br&gt; 0.12–0.17 (Cu)</td>
<td></td>
</tr>
</tbody>
</table>
Hair of cow (30) 1.33 ± 0.07 7.3 ± 0.2 13.3 (Mo)
Blood of cow (20) 0.035 ± 0.07 0.61 ± 0.09 3.2 (Mo)

**Background areas (Baksan, Kizburun, Chegem, Aushiger)**

<table>
<thead>
<tr>
<th></th>
<th>Water (9)</th>
<th>Soil (12)</th>
<th>Hay crop of plants (12)</th>
<th>Hair of cow (30)</th>
<th>Blood of cow (20)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0004–0.001</td>
<td>2.0–2.4</td>
<td>0.5–3.2</td>
<td>0.1 ± 0.02</td>
<td>0.011 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>0.001–0.0016</td>
<td>10.6–31.7</td>
<td>1.8–12.4</td>
<td>7.6 ± 0.3</td>
<td>1.03 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>0.25–1.33 (Mo)</td>
<td></td>
<td>0.16–0.39 (Cu)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

EC in soils of the Chegem-river valley makes 1.2 for Mo and 7.7 for W. In soil of both regions of investigation the concentration of Zn is increased (EC 2.7 for Baksans valley and 2.2 – for Chegems valley). The quantity of Mo and Cu is some more higher in some plants. However, if the molybdenum content is increased in blood, milk and hair of cows, the level of copper significantly reduced compared with control animals areas.

Indicated metals were detected not only in cow milk, but in buttermilk too. При этом Their content is increased in buttermilk in 5–10 times as in mine areas, as in background sites herewith. So, the buttermilk of control site (Kudinovo) contained (in µg/l): Cu – 130, Mo – 93, W – 4, and in the product from cow milk from Tyrnyauz: Cu – 556, Mo – 684, W – 43 µg/l.

Taking into account known connection of molybdenum with the xanthine-oxidase, this enzyme was isolated from the buttermilk of animals from background territory (Kudinovo). It was discovered two fraction of this enzyme, predominantly containing Mo and Cu or Mo and W (Fig. 1).

**Fig. 1.** Variation of concentration of metals, protein and activity of xanthine-oxidase in the fractions of prepared enzyme

Thus, in during biogeochemical investigations of W–Mo mine landscapes of the North Caucasus (Tyrnyauz) and background territories was discovered the accumulation of tungsten not only plant or soil microorganisms, but the including of this element in animal enzyme xanthine-oxidase. At increasing of molybdenum and tungsten level in the environment, the migration of last metal is enhancing very hard at mine areas.
ERMAKOV ET AL.: DIFFERENTIATION OF COPPER, MOLYBDENUM

Supported by grant of RFBR No. 12-05-00141-a.

References
