Review Article
The Exploration Significance of Ag/Au, Au/Cu, Cu/Mo, (Ag×Au)/(Cu×Mo) Ratios, Supra-ore and Sub-ore Halos and Fluid Inclusions in Porphyry Deposits: A Review

H. Atapour*

Department of Mining Engineering, Faculty of Engineering, Shahid Bahonar University of Kerman, P.O.Box 76169-133, Kerman, Islamic Republic of Iran

Received: 13 April 2016 / Revised: 21 August 2016 / Accepted: 26 October 2016

Abstract
This paper documents the exploration significance of Ag/Au, Au/Cu, Cu/Mo and (Ag×Au)/(Cu×Mo) ratios of the supra-ore and sub-ore halos versus fluid inclusion evolution for 24 Cu, 6 Cu–Mo and 10 Cu–Au porphyry deposits worldwide. The ratios are based only on the economic and mineralized hypogene alteration zones. The results indicate that (Ag×Au)/(Cu×Mo), Au/Cu and Cu/Mo ratios increase with decreasing depth and could be considered as the possible exploration guides for many as-yet undiscovered unexposed porphyry deposits. These ratios are well correlated with vertical elemental vector zoning and alteration halos from the center (proximal potassic) outward (distal propylitic-zeolitic) and follow the order of Cu-Mo-Au, Cu-Zn, Zn-Pb-Ag, Ag-Pb-As-Sb-Hg-Au. On the basis of the (Ag×Au)/(Cu×Mo) ratios and fluid inclusion data, the Iranian continental arc porphyry copper deposits show multiphase halite-sylvite saturated fluid inclusions and formed between 2 to 4.75 km depth. The simple and multiple geochemical ratios and fluid inclusion evolution highlight that the Cu, Cu-Mo and Cu-Au porphyry deposits of the world were probably formed at <8-0.6, <5-2 and <4-1 km, respectively. This depth zoning could be used as an exploration target for hypogene as well as supergene mineralized zones, vectoring the position of ore body with respect to the primary halos or even level of erosion for unexposed porphyry systems. The main factors controlling the elemental ratios are related to the depth of mineralization, hydrothermal complexing of metal ligands and the presence or absence of sulfides minerals and gold-silver alloys.

Keywords: Geochemical ratios; Fluid inclusions; Depth of porphyry Cu; Cu-Mo; Cu-Au deposits.

Introduction
The exploration significance of Ag/Au, Au/Cu, Cu/Mo, and (Ag×Au)/(Cu×Mo) elemental ratios and fluid inclusion evolution in relation to depth of formation in porphyry and hydrothermal deposits is

* Corresponding author: Tel: +983432114041-9; Fax: +983432121003; Email: atapour@uk.ac.ir

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poorly documented, though many porphyry systems show a centrally copper-rich proximal zone surrounded by Zn-Pb-Au-Ag distal aureole zone [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45]. Experimental studies by Simon et al. [46], in the Cu-Fe-S system at 400 to 700°C indicate that most of the gold will be deposited in the high-temperature bornite-rich porphyry copper-gold deposits. Murakami et al. [47], reexamined valuable published data only on the Cu/Au ratios as an indication of formation depth of porphyry-style Cu-Au-Mo deposits, but their results have met with mixed success and overlapping of the similar Cu/Au ratios with different depths of porphyry ore formation, thus, the Cu/Au ratios gives some limitations. The main limitation is that copper could not display the role of a numerator, because its halos form before gold halos in the high temperature hydrothermal ores, thus the correct ratio should be presented as Au/Cu. According to Beus and Grigorian [48], the first prerequisite for the use of elemental ratios in hypogene hydrothermal depth zoning and supergene oxidation zone is related to the elements that form supra-ore halos in the low temperature shallow zones (e.g., Ag, Au) and sub-ore halos in the high temperature deeper zones (e.g., Cu, Mo). The standard elemental zoning proposed by Beus and Grigorian [48], follow vertically from the supra-ore halos (shallower) to the sub-ore halos (greater depth) as: Ba-Sb-As-Hg-Cd-Ag-Pb-Zn-Cu-Bi-Mo-Co-Ni-U-Sn-Be-W. In this regard, vertical zonation of supra-ore and sub-ore halos could assess the position of the ore body with respect to the primary hypogene halos as well as the exposed level of erosion of geochemical anomalies [48].

The exploration use of Ag/Au, Au/Cu, Cu/Mo and (Ag×Au)/(Cu×Mo) has not been fully explored by the previous studies. The approaches in this paper are: (1) to assess the geochemical significance of the Ag/Au, Au/Cu, Cu/Mo ratios and a newly proposed (Ag×Au)/(Cu×Mo) ratio for exploration guides, and (2) present fluid inclusion data as a complementary possible exploration tool for the economic hypogene Cu, Cu-Mo and Cu-Au deposits worldwide.

Global distribution and tectonomagmatic aspects of porphyry deposits

Porphyry deposits form linear and narrow metallogenic provinces [49] with large, medium-to low grade deposits worldwide (Fig. 1) that are associated with Mesozoic to Cenozoic orogenic belts.

Figure 1. Approximate position of some Cu, Cu-Mo and Cu-Au porphyry deposits of the world (modified after [49, 50, 52, 53]).
Table 1. Tectonomagmatic and petrogeochemical aspects of some important porphyry deposits worldwide. (modified after [17, 49, 50, 52, 53]).

<table>
<thead>
<tr>
<th>Porphyry deposits</th>
<th>Mo/Cu</th>
<th>SiO₂(%)</th>
<th>Productive intrusive rocks</th>
<th>Tectonic setting</th>
<th>Magmatic affinity</th>
<th>Potential byproducts</th>
<th>Exploration guides</th>
<th>Global examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>&lt; 0.1</td>
<td>55-70</td>
<td>Diorite, granodiorite, quartz monzonite, tonalite and granite</td>
<td>Continental arc (flat – moderate subduction angles)</td>
<td>Calalkaline, potassic calalkaline and shoshonitic ± adakitic</td>
<td>Mo, Re, Au and Ag</td>
<td>Gossan, GS, RS, IP, soil, mesquite and alluvial sampling</td>
<td>Sarcheshmeh (Iran) and El-Salvador (Chile)</td>
</tr>
<tr>
<td>Cu-Mo</td>
<td>0.1</td>
<td>55-70</td>
<td>Monzonite, quartz monzodiorite, monzogranite and granite</td>
<td>Continental arc</td>
<td>Calalkaline, potassic calalkaline and shoshonitic</td>
<td>Au and Ag</td>
<td>Gossan, RS, soil and alluvial sampling</td>
<td>Chuquicamata (Chile) and Bingham (America)</td>
</tr>
<tr>
<td>Cu-Au</td>
<td>&lt; 0.01</td>
<td>55-65</td>
<td>Diorite, syenite and monzodiorite</td>
<td>Island arc, post collisional arc</td>
<td>Potassic calalkaline, shoshonitic and adakitic</td>
<td>Ag and PGE</td>
<td>Gossan, heavy minerals, soil and alluvial sampling for gold</td>
<td>Grasberg (Indonesia) and Kenses (Canada)</td>
</tr>
<tr>
<td>Mo</td>
<td>&gt;1</td>
<td>65-74 or &gt;74</td>
<td>Syenite, quartz monzonite, A-type granite and rhyolite</td>
<td>Anorogenic extensional rifting</td>
<td>Alkaline and calalkaline</td>
<td>W and Sn</td>
<td>Aeromagnet ic, and soil sampling for F-and W</td>
<td>Climax and Mount Emmons (America)</td>
</tr>
<tr>
<td>Au</td>
<td>&lt; 0.001</td>
<td>55-65</td>
<td>Diorite and syenite and quartz syenite</td>
<td>Island arc ± continental arc</td>
<td>Alkaline, shoshonic and calalkaline</td>
<td>Ag, Cu and Mo</td>
<td>Gossan, heavy minerals and soil sampling</td>
<td>Troilus (Canada) and Sulat (Philippines)</td>
</tr>
</tbody>
</table>

in western North and South America, around the western margin of the Pacific Rim, Europe, Central Asia, Middle East, major deposits in Paleozoic orogens of Central Asia and eastern North America and minor occurrences within Precambrian terrains [49, 50, 51, 52, 53]. They consist of composite stocks with typical porphyry textures and are formed in different tectonomagmatic settings, have diverse magmatic affinity and contain variable values of Cu, Mo, Au, Ag and potential byproducts (Table 1). Also, in Figure 2 some of the most important Iranian continental arc porphyry copper deposits are shown.

Materials and Methods

Importantly, the geochemical data on Ag/Au, Au/Cu, Cu/Mo, and (Ag×Au)/(Cu×Mo) ratios and bulk grade of economic porphyry deposits and or mines hosted by hypogene alteration zones are very limited worldwide (e.g., [23, 47, 53, 54, 55]). In fact, precise and accurate Cu and Mo values in hypogene mineralized zones are reported for most of the economic porphyry deposits worldwide, but their Au, Ag and other metal contents, in particular formation depth and other factors could not be easily collected for this study by the author. This study excludes the geochemical data from the oxidation or supergene zones. Despite the limited geochemical data in this paper, important geochemical and fluid inclusion data on some of the Iranian porphyry copper deposits is presented [56, 57, 58, 59, 60]. However, some valuable geochemical data (e.g., [55, 60]) have been republished by Murakami et al. [47]; and Voudouris et al. [23]. In addition to these previously published data, new data are introduced on formation depth from some important Iranian continental arc porphyry copper deposits. The available existing geochemical data worldwide include about 24 Cu porphyry, 6 Cu-Mo porphyry and 10 Cu-Au (Table 2, 3 and 4) were selected from Canada (17), Iran (8), United State of America (6), Chile (6), Philippines (20), Kazakhstan (1), Argentinia (1) and Armenia (1), respectively. Total tonnage, grades of Cu, Au, Mo and Ag and data on formation depth were compiled from the published compilations [17, 46, 47, 50, 53, 54, 55, 56, 57, 61, 62, 63, 64]. The main approach in this study is to compare the possible exploration significance of Ag/Au atomic mass, Au/Cu atomic mass × 10000, Cu/Mo atomic mass and (Ag×Au)/(Cu×Mo) atomic mass ratios in different types of porphyry deposits. The use of (Ag×Au)/(Cu×Mo) smooths out erratic analytical and sampling errors, thus allows a better
estimate of formation depth and exploration zoning than those of simple elemental ratios (Beus and Grigorian [48]).

**Results and Discussion**

The results of revised geochemical data on Ag/Au, Au/Cu×10000, Cu/Mo, and (Ag×Au)/(Cu×Mo) ratios are indicated in Table 2, 3 and 4 and also in Figure 3, 4 and 5 respectively. Accordingly, the highest Au/Cu, Cu/Mo and (Ag×Au)/(Cu×Mo) ratios are related to Cu porphyries and Cu-Au porphyry rather than Cu-Mo porphyry deposits. This might be related to the formation of immiscible sulfide liquids during crystallization of parent magma as has been reported by Simon et al. [46]. However, the highest Ag/Au ratios are developed in Cu and Cu-Mo porphyries. This is reflected to the lower gold contents in Cu-Mo porphyries [21]. According to Fig. 3, 4 and 5, the (Ag×Au)/(Cu×Mo) and Cu/Mo ratios increase with decreasing depth and vice versa in all types of porphyry deposits. The Ag/Au ratios increase with increasing depth in both Cu and Cu-Mo porphyries.

*Figure 2.* Geological map of Iran, showing the approximate position of some important continental arc porphyry copper deposits (modified after [50, 56, 57]). 1- Darrehamzeh, 2- Zaminhosien, 3- Darrehalu, 4- Sarcheshme, 5- Gode Kolvary, 6- Abdar, 7- Miduk, 8- Soungoun.
Table 2. Tonnage, grade, Ag/Au, Au/Cu, Cu/Mo, (Ag×Au)/(Cu×Mo) ratios in relation to formation depth of the selected Cu porphyry deposits.

| Deposit (country) | Tonnage (Mt) | Cu (%) | Mo (%) | Ag (g/t) | Au (g/t) | Ag/Au | Au/Cu *10000 | Cu/Mo | Ag*Au/Cu*Mo | Forma
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bethlehem (Canada)</td>
<td>677</td>
<td>0.45</td>
<td>0.016</td>
<td>0.4</td>
<td>0.005</td>
<td>80</td>
<td>111</td>
<td>28.00</td>
<td>0.28</td>
<td>3.9</td>
</tr>
<tr>
<td>Valley Copper (Canada)</td>
<td>800</td>
<td>0.48</td>
<td>0.01</td>
<td>1.9</td>
<td>0.006</td>
<td>316</td>
<td>125</td>
<td>48.00</td>
<td>2.38</td>
<td>4.8</td>
</tr>
<tr>
<td>Lornex (Canada)</td>
<td>514</td>
<td>0.43</td>
<td>0.015</td>
<td>1.2</td>
<td>0.006</td>
<td>200</td>
<td>139</td>
<td>28.00</td>
<td>1.12</td>
<td>4.4</td>
</tr>
<tr>
<td>Highmont (Canada)</td>
<td>265</td>
<td>0.27</td>
<td>0.041</td>
<td>0.9</td>
<td>0.004</td>
<td>225</td>
<td>148</td>
<td>7.00</td>
<td>0.33</td>
<td>3.9</td>
</tr>
<tr>
<td>Gibraltar (Canada)</td>
<td>965</td>
<td>0.32</td>
<td>0.01</td>
<td>0.9</td>
<td>0.07</td>
<td>12.85</td>
<td>2187</td>
<td>32.00</td>
<td>19.69</td>
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<td>0.009</td>
<td>1.1</td>
<td>0.12</td>
<td>9.16</td>
<td>2790</td>
<td>48.00</td>
<td>34.11</td>
<td>1.2</td>
</tr>
<tr>
<td>Island Copper (Canada)</td>
<td>377</td>
<td>0.41</td>
<td>0.017</td>
<td>1.4</td>
<td>0.19</td>
<td>7.5</td>
<td>4634</td>
<td>24.00</td>
<td>38.16</td>
<td>1.5</td>
</tr>
<tr>
<td>Schaft Creek (Canada)</td>
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<td>0.3</td>
<td>0.033</td>
<td>1.2</td>
<td>0.14</td>
<td>9</td>
<td>4667</td>
<td>9.00</td>
<td>16.97</td>
<td>0.6</td>
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<tr>
<td>Morrison (Canada)</td>
<td>190</td>
<td>0.4</td>
<td>0.017</td>
<td>1</td>
<td>0.21</td>
<td>5</td>
<td>5250</td>
<td>24.00</td>
<td>30.88</td>
<td>1.2</td>
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<tr>
<td>Ann Mason (America)</td>
<td>495</td>
<td>0.4</td>
<td>0.01</td>
<td>0.001</td>
<td>0.01</td>
<td>0.1</td>
<td>250</td>
<td>40.00</td>
<td>0.03</td>
<td>3.3</td>
</tr>
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<td>Butte (America)</td>
<td>5220</td>
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<td>8.6</td>
<td>0.042</td>
<td>204</td>
<td>627</td>
<td>24.00</td>
<td>19.25</td>
<td>7.5</td>
</tr>
<tr>
<td>Santa Rita (America)</td>
<td>3030</td>
<td>0.47</td>
<td>0.008</td>
<td>1.4</td>
<td>0.056</td>
<td>25</td>
<td>1191</td>
<td>59.00</td>
<td>20.85</td>
<td>6.3</td>
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<tr>
<td>Ely (America)</td>
<td>754</td>
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<td>0.01</td>
<td>0.8</td>
<td>0.27</td>
<td>3</td>
<td>4427</td>
<td>61.00</td>
<td>35.41</td>
<td>3.4</td>
</tr>
<tr>
<td>El Salvador (Chile)</td>
<td>866</td>
<td>1.41</td>
<td>0.01</td>
<td>1.5</td>
<td>0.12</td>
<td>12.5</td>
<td>851</td>
<td>141.00</td>
<td>12.77</td>
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</tr>
<tr>
<td>Agua Rica (Armenia)</td>
<td>1710</td>
<td>0.43</td>
<td>0.032</td>
<td>3.2</td>
<td>0.17</td>
<td>19</td>
<td>3953</td>
<td>14.00</td>
<td>39.53</td>
<td>2.6</td>
</tr>
<tr>
<td>Aktopgai (Kazakhstan)</td>
<td>3200</td>
<td>0.39</td>
<td>0.008</td>
<td>1.1</td>
<td>0.029</td>
<td>38</td>
<td>744</td>
<td>49.00</td>
<td>10.22</td>
<td>2.1</td>
</tr>
<tr>
<td>Sarcheshmeh (Iran)</td>
<td>450</td>
<td>1.13</td>
<td>0.03</td>
<td>3.9</td>
<td>0.11</td>
<td>35</td>
<td>973</td>
<td>37.00</td>
<td>12.6</td>
<td>4.75</td>
</tr>
<tr>
<td>Miduk (Iran)</td>
<td>170</td>
<td>0.82</td>
<td>0.007</td>
<td>1.8</td>
<td>0.082</td>
<td>22</td>
<td>1000</td>
<td>117.00</td>
<td>25</td>
<td>2.51</td>
</tr>
<tr>
<td>Atsoungoun (Iran)</td>
<td>600</td>
<td>0.76</td>
<td>0.01</td>
<td>2.2</td>
<td>0.017</td>
<td>129</td>
<td>223</td>
<td>76.00</td>
<td>10</td>
<td>2.1</td>
</tr>
<tr>
<td>Abdar or Mosahim (Iran)</td>
<td>-</td>
<td>0.43</td>
<td>0.009</td>
<td>1.6</td>
<td>0.085</td>
<td>18</td>
<td>1976</td>
<td>47.00</td>
<td>35</td>
<td>2.85</td>
</tr>
<tr>
<td>Gode Kolvar (Iran)</td>
<td>-</td>
<td>0.1</td>
<td>0.001</td>
<td>0.57</td>
<td>0.023</td>
<td>24</td>
<td>2300</td>
<td>100.00</td>
<td>131</td>
<td>2</td>
</tr>
<tr>
<td>Darrehala (Iran)</td>
<td>25</td>
<td>0.46</td>
<td>0.0065</td>
<td>1.44</td>
<td>0.034</td>
<td>42</td>
<td>739</td>
<td>70.00</td>
<td>16</td>
<td>2.1</td>
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<td>Zaminhosien or Babnam (Iran)</td>
<td>-</td>
<td>0.28</td>
<td>0.0003</td>
<td>0.98</td>
<td>0.07</td>
<td>14</td>
<td>2600</td>
<td>933.00</td>
<td>816</td>
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<tr>
<td>Darrehhamzeh (Iran)</td>
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<td>0.1</td>
<td>0.0008</td>
<td>2.4</td>
<td>0.059</td>
<td>40</td>
<td>5900</td>
<td>12.50</td>
<td>1770</td>
<td>2.4</td>
</tr>
</tbody>
</table>


probably indicating the presence of silver sulfosalts and electrum. In Cu-Au porphyries, the Ag/Au ratios increase with decreasing depth. There are no enough data on zoning aspects of the Ag/Au ratios in porphyry deposits. However, Einaudi [5] reported a systematic increase of Ag/Au ratios toward the surface in Bingham porphyry copper mining district. The Au/Cu ratios in Cu porphyries increase from 111 to 5900 with
decreasing depth. This is likely related to the ubiquitous presence of chalcopyrite at the greater depth of porphyry copper deposits [65]. Moreover, according to these authors, deep-seated porphyry copper-molybdenum deposits are deficient in gold values, contain higher modal contents of chalcopyrite and show lower Au/Cu ratios. At shallower depth, due to the presence of S and Au-rich vapor phase, the Au/Cu ratio will increase [65].

Cu/Mo ratios follow zoning patterns of sub-ore and supra-ore halos and depth zoning [48]. As such, the Cu/Mo ratios in in Cu, Cu/Mo and Cu-Au porphyry deposits decrease with increasing depth. This indicates that molybdenite-rich porphyries are formed between 370-440 °C at greater depth and under low hydrostatic pressures [66].

In Cu-Au porphyry deposits (Table 4), the formation depth for majority of the deposits does not vary significantly (e.g., 0.9 to 1.2 km). However, Ag/Au, Cu/Mo and (Ag×Au)/(Cu×Mo) ratios increase with decreasing depth. This may be due to the higher values of Cu, Ag and Cu and lower contents of Mo in

<table>
<thead>
<tr>
<th>Deposit (country)</th>
<th>Tonnage (Mt)</th>
<th>Cu (%)</th>
<th>Mo (%)</th>
<th>Ag(g/t)</th>
<th>Au(g/t)</th>
<th>Ag/Au</th>
<th>Au/Cu×10000</th>
<th>Cu/Mo</th>
<th>Ag<em>Au/Cu</em>Mo</th>
<th>Cu/Au×10000</th>
<th>Formation depth (km)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Huckleberry (Canada)</td>
<td>161</td>
<td>0.48</td>
<td>0.015</td>
<td>0.93</td>
<td>0.025</td>
<td>156</td>
<td>521</td>
<td>32</td>
<td>3.23</td>
<td>2.3</td>
<td>1, 2</td>
<td></td>
</tr>
<tr>
<td>Brenda (Canada)</td>
<td>227</td>
<td>0.16</td>
<td>0.039</td>
<td>0.63</td>
<td>0.013</td>
<td>49</td>
<td>8125</td>
<td>4</td>
<td>1.31</td>
<td>4.4</td>
<td>1, 2</td>
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<td>Berg (Canada)</td>
<td>250</td>
<td>0.4</td>
<td>0.03</td>
<td>5</td>
<td>0.05</td>
<td>100</td>
<td>1250</td>
<td>14</td>
<td>20.83</td>
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<td>Mineral Park (America)</td>
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<td>0.46</td>
<td>0.032</td>
<td>2.2</td>
<td>0.027</td>
<td>82</td>
<td>587</td>
<td>15</td>
<td>4.04</td>
<td>4.4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Chuquicamata (Chile)</td>
<td>17100</td>
<td>0.65</td>
<td>0.04</td>
<td>5</td>
<td>0.013</td>
<td>384</td>
<td>200</td>
<td>16</td>
<td>2.50</td>
<td>4.5</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Bingham (America)</td>
<td>3230</td>
<td>0.88</td>
<td>0.053</td>
<td>3.3</td>
<td>0.38</td>
<td>9</td>
<td>4318</td>
<td>17</td>
<td>30</td>
<td>2.5</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Tonnage, grade, Ag/Au, Au/Cu×10000, Cu/Mo and (Ag×Au)/(Cu×Mo) ratios in relation to formation depth of the selected Cu-Mo porphyry deposits.

<table>
<thead>
<tr>
<th>Deposit (country)</th>
<th>Tonnage (Mt)</th>
<th>Cu (%)</th>
<th>Mo (%)</th>
<th>Ag(g/t)</th>
<th>Au(g/t)</th>
<th>Au/Cu×10000</th>
<th>Cu/Mo</th>
<th>Ag<em>Au/Cu</em>Mo</th>
<th>Cu/Au×10000</th>
<th>Formation depth (km)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laescondida (Chile)</td>
<td>4860</td>
<td>0.97</td>
<td>0.00</td>
<td>5</td>
<td>0.25</td>
<td>20</td>
<td>2577</td>
<td>161</td>
<td>214.78</td>
<td>38,800</td>
<td>3.2</td>
</tr>
<tr>
<td>Copper Mountain (Canada)</td>
<td>324</td>
<td>0.47</td>
<td>0.00</td>
<td>3.9</td>
<td>0.17</td>
<td>23</td>
<td>3617</td>
<td>470</td>
<td>1410.64</td>
<td>27647</td>
<td>1.1</td>
</tr>
<tr>
<td>Bell (Canada)</td>
<td>495</td>
<td>0.36</td>
<td>0.00</td>
<td>1</td>
<td>0.16</td>
<td>6.25</td>
<td>4444</td>
<td>72</td>
<td>88.89</td>
<td>22,500</td>
<td>1.2</td>
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<tr>
<td>Tanana (Alaska)</td>
<td>126</td>
<td>0.64</td>
<td>0.00</td>
<td>1</td>
<td>0.38</td>
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<td>8260</td>
<td>92</td>
<td>201.88</td>
<td>16,842</td>
<td>3</td>
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<tr>
<td>Iron Max (Ajax) (Canada)</td>
<td>21</td>
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<td>0.00</td>
<td>2</td>
<td>0.34</td>
<td>6</td>
<td>3445</td>
<td>450</td>
<td>1511.11</td>
<td>13,235</td>
<td>0.9</td>
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<tr>
<td>Galore Creek (Canada)</td>
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<td>0.68</td>
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<td>0.52</td>
<td>7.9</td>
<td>3676</td>
<td>680</td>
<td>6041.18</td>
<td>13,077</td>
<td>1.2</td>
</tr>
<tr>
<td>Kadzharan (Armenia)</td>
<td>181</td>
<td>0.65</td>
<td>0.05</td>
<td>2</td>
<td>0.65</td>
<td>3</td>
<td>10000</td>
<td>13</td>
<td>40.00</td>
<td>10,000</td>
<td>1.5</td>
</tr>
<tr>
<td>Carribo Bell (Canada)</td>
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<td>0.23</td>
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<td>1</td>
<td>0.3</td>
<td>4</td>
<td>13043</td>
<td>230</td>
<td>5217.39</td>
<td>7666</td>
<td>1</td>
</tr>
<tr>
<td>Santo Tomas (Philippines)</td>
<td>449</td>
<td>0.38</td>
<td>0.00</td>
<td>1</td>
<td>0.7</td>
<td>2</td>
<td>18421</td>
<td>380</td>
<td>2763.16</td>
<td>5,428</td>
<td>2</td>
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</tbody>
</table>

Table 4. Tonnage, grade, Ag/Au, Au/Cu×10000, Cu/Mo and (Ag×Au)/(Cu×Mo) ratios in relation to formation depth of the selected Cu-Au porphyry deposits.

1: [47, 55], 2: [7], 3: [18, 47], 4: [10].

Cu/Mo ratios in in Cu, Cu/Mo and Cu-Au porphyries decrease with increasing depth. This indicates that molybdenite-rich porphyries are formed between 370-440 °C at greater depth and under low hydrostatic pressures [66].

In Cu-Au porphyry deposits (Table 4), the formation depth for majority of the deposits does not vary significantly (e.g., 0.9 to 1.2 km). However, Ag/Au, Cu/Mo and (Ag×Au)/(Cu×Mo) ratios increase with decreasing depth. This may be due to the higher values of Cu, Ag and Cu and lower contents of Mo in
Cu-Au porphyries. Au/Cu ratios do not show a well defined trend with depth.

In contrast to the simple Ag/Au, Au/Cu and Cu/Mo ratios, the use of multiplicative (Ag×Au)/(Cu×Mo) ratios give the best significant results, as the ratios for Cu, Cu-Mo and Cu-Au porphyry deposits increase with decreasing formation depth. This shows the potential role of Ag and Au supra-ore halos toward the surficial parts of the Cu, Cu-Mo and Cu-Au porphyries, thus could be considered as an exploration

Figure 3. Relationship between Ag/Au (a), Au/Cu (b), Cu/Mo (c) and Ag×Au/Cu×Mo (d) ratios and formation depth of the Cu porphyry deposits.

Figure 4. Relationship between Ag/Au (a), Au/Cu (b), Cu/Mo (c) and (Ag×Au)/(Cu×Mo) (d) ratios and formation depth of the Cu-Mo porphyry deposits.
guide for prospecting unexposed porphyry deposits.

Beus and Grigorian [48] assume that for vertical zonation of supra-ore and sub-ore halos, the composition of hydrothermal fluids remains constant with time, but the depth of ore formation to be the main controlling factor. However, some minor factors could slightly influence the elemental ratios. These may include tectonic setting, lithology, pH-Eh and transporting ligands for metal complexes, respectively. Table 1 shows that continental arc Cu and Cu-Mo porphyries, postcollisional or Island arc Cu-Au porphyries and anorogenic Mo porphyries form in different tectonic settings. However, their Au/Cu, Cu/Mo and (Ag×Au)/(Cu×Mo) ratios (Fig. 3, 4 and 5) show the same increasing trend toward the surficial parts of the deposits. Although the chemical composition of productive intrusive rocks in terms of SiO₂ (Table 1) does not differ significantly, the Au/Cu, Cu/Mo and (Ag×Au)/(Cu×Mo) ratios display an increasing trend toward the shallower depth. In case that the composition of hydrothermal fluids changes with time [48], the zoning sequence may be controlled by hydrothermal transporting ligands. For example in most high temperature conditions (> 400 or 450 to 500 °C) and acidic pH (4-5), high contents of Cu and Au are transported by chloride complexes of hypersaline fluids, which after cooling form considerable amounts of chalcopyrite-gold values in porphyry deposits [65]. This might influence the Au/Cu ratios, but there are no enough data to discuss this point. In contrast to this, below 400 °C, H₂S-rich solutions could transport and increase the solubility of gold to 1-10 ppm [65], but would not be able to transport considerable copper (< 1 ppm). Presumably, in this condition, the Au/Cu ratios will increase toward the low temperature zones or surficial part of the porphyry deposits. Also, the sulfide mineralogy could change the Au/Cu ratios in bornite or pyrrhotite-rich porphyry deposits [65]. Crystallization of pyrrhotite and bornite remove copper from the melt at a higher rate than it can remove gold, thus increasing the Au/Cu ratios [66]. The sequential deposition of molybdenite followed by chalcopyrite may change the Cu/Mo ratios in porphyry deposits. In this regard, molybdenite could precipitate before sericitic alteration in response to decreasing pH, but chalcopyrite is usually formed at lower temperatures during fluid neutralization [66]. This is consistent with the increasing trend of Cu/Mo ratios (Fig. 3, 4 and 5) toward the shallower depth in all porphyry deposits. Furthermore, the low Cu/Mo ratios in Mo-rich porphyry deposits are probably controlled by

Figure 5. Relationship between Ag/Au (a), Au/Cu (b), Cu/Mo (c) and (Ag×Au)/(Cu×Mo) (d) ratios and formation depth of the Cu-Au porphyry deposits.
Table 5. Geological, mineralogical, geochemical, tonnage grade, elemental ratios and estimated formation depth (fluid inclusion) of some important Miocene continental arc porphyry copper deposits, Iran.

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Volcanic rocks (Eocene)</th>
<th>Granitoid rocks (Miocene)</th>
<th>Hypogene Mineralization-alteration</th>
<th>Tonnage (Mt)</th>
<th>Cu (%)</th>
<th>Mo (%)</th>
<th>Ag (g/t)</th>
<th>Au (g/t)</th>
<th>Ag/Au</th>
<th>Cu/Mo</th>
<th>Cu/Cu*</th>
<th>Forma- tion depth (km)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sarcheshmeh</td>
<td>Trachybasalt and trachyandesite</td>
<td>Quartz monzonite and granodiorite</td>
<td>Py, Cp, Mol, Sph, Po, Ga, Py/Cp = 12, Potassic-phyllitic</td>
<td>450</td>
<td>1.13</td>
<td>0.03</td>
<td>3.9</td>
<td>0.11</td>
<td>35</td>
<td>37</td>
<td>973</td>
<td>12.6</td>
<td>4.75</td>
</tr>
<tr>
<td>Miduk</td>
<td>Trachybasalt and basaltic andesite</td>
<td>Diorite and quartz diorite</td>
<td>Py, Cp, Mol, Py/Cp = 3.12, Potassic-phyllitic</td>
<td>170</td>
<td>0.82</td>
<td>0.007</td>
<td>1.8</td>
<td>0.082</td>
<td>22</td>
<td>117</td>
<td>1000</td>
<td>25</td>
<td>2.51</td>
</tr>
<tr>
<td>Soungoun</td>
<td>Dacite and trachyandesite</td>
<td>Monzonite and quartz monzonite</td>
<td>Py, Cp, Mo, Py/Cp = 2-12, Potassic-phyllitic</td>
<td>600</td>
<td>0.76</td>
<td>0.01</td>
<td>2.2</td>
<td>0.017</td>
<td>129</td>
<td>76</td>
<td>223</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Abdar (Mosahim)</td>
<td>Dacite and trachyandesite</td>
<td>Diorite and quartz diorite</td>
<td>Py, Cp, Ga, Sph, Mol, Py/Cp = 16, Potassic-phyllitic</td>
<td>-</td>
<td>0.43</td>
<td>0.009</td>
<td>1.6</td>
<td>0.085</td>
<td>18</td>
<td>47</td>
<td>1976</td>
<td>35</td>
<td>2.85</td>
</tr>
<tr>
<td>Gode-Kolvary</td>
<td>Trachybasalt and trachyandesite</td>
<td>Diorite and quartz diorite</td>
<td>Py, Cp, Mol, Py/Cp = 12, Potassic-phyllitic</td>
<td>-</td>
<td>0.1</td>
<td>0.001</td>
<td>0.57</td>
<td>0.023</td>
<td>24</td>
<td>100</td>
<td>2300</td>
<td>131</td>
<td>2</td>
</tr>
</tbody>
</table>

1: [58], 2: [60], 3: [59], 4: [59], 5: [8], 6: [50], 7: [57], 8: [51]. Py= pyrite, Cp= chalcopyrite, Mol= molybdenite, Ga= galena and Sph= sphalerite and Po= pyrrhotite.

The Exploration Significance of Ag/Au, Au/Cu, Cu/Mo, (Ag×Au)/(Cu×Mo) Ratios, …

Considerable high oxygen fugacity in such fluids, thus Fe is a major component of such solutions, together with Na and K similar to those reported by Bodnar [67]. The interpretation of fluid inclusion data from Gode Kolvari porphyry copper deposit in Iran is shown in Table 5, Fig. 6c and 6d and by the use of P-X and P-T phase diagram in NaCl-H₂O system (Fig. 7). The highest homogenization temperature was found to be around 600 °C with salinity of about 70 wt % NaCl equivalent (Fig. 6d), corresponding to potassic alteration. Furthermore, the presence of chalcopyrite crystals in fluid inclusions supports the granitoid related fluids of magmatic origin, in particular of potassic-phyllitic alteration zone. According to the geological reconstruction of the area [50, 63], the total estimated stratigraphic thickness of the overlying rocks at the time of porphyry intrusive emplacement at Gode Kolvari porphyry system is estimated to have been about 2 km, which corresponds to a lithostatic pressure of about 500 bars or a hydrostatic pressure of 200 bars. Therefore, the maximum formation depth of the Miocene Gode Kolvari porphyry copper deposit is about 2 km. The exploration significance of formation depth in continental arc porphyry copper deposits of Iran is indicated in Table 5. The Sarcheshmeh deposit has been reported to have been formed at 4.75 km depth [58, 60].

Possible exploration model

The relationship between elemental ratios with thiomolybdate-sodium complexes, low chlorine concentrations and high fugacity of H₂O [66].

Fluid inclusion evolution versus elemental ratios and formation depth.

According to Bodnar [67], pressure release via lithostatic to hydrostatic transition causes the fluid phase separation into brine and vapour phases. This will result in a wide range in the fluid inclusion salinities (0 - 70 wt % NaCl equivalent), homogenization temperatures (200 - 700 °C) and formation depth (1-7km) for different porphyry deposits. Geological, mineralogical, geochemical, elemental ratios and formation depth of some important Iranian continental arc porphyry copper deposits are shown in Table 5. The most distinguishing feature of the fluid inclusion data in some of the Iranian porphyry copper deposits, is the common occurrence of highly saline inclusions scheme of Bodnar [67], containing multiple daughter minerals including halite, sylvinite, hematite and chalcopyrite. Figure 6a illustrates an example of multiphase halite – saturated fluid inclusion in Gode Kolvari Miocene porphyry copper deposit. These types of fluid inclusions coexist with low density vapor phase, thus have been formed by the liquid-vapor phase separation of an intrinsic part of the magmatic-hydrothermal evolution.

The common occurrence of halite and hematite as daughter minerals of magmatic-related inclusions (Fig. 6b) indicates the high level of dissolved Fe and...
formation depth and their regional or detail exploration potential in porphyry deposits has not been fully explored in the literatures. In this paper, we discuss the exploration significance of the Ag/Au, Au/Cu, Cu/Mo and (Ag\times Au)/(Cu\times Mo) ratios in three different types of porphyry deposits.

In Cu, Cu-Mo and Cu-Au porphyry deposits, the Au/Cu, Cu/Mo and (Ag\times Au)/(Cu\times Mo) ratios display an increasing trend with decreasing depth. This indicates the presence of the argentite, silver bearing sulfosalts, electrum and gold in the shallowest part of the porphyry deposits, probably in the phyllic, propylitic and advanced argillic ore zone. It also indicates that most of the Cu and Mo ores is formed in the deepest zone of potassic-sericitic alteration as suggested by Chaffee [68]. The higher Au/Cu ratios may reflect that the gold grade increases toward surface, indicating the role of S-rich bisulfide complexes below 300°C and enrichment of gold at low-temperature zones [55, 65].

The Ag/Au ratios in selected porphyry Cu and Cu-Mo deposits increase with increasing depth. This is possibly related to the role of silver chloride complexes at higher temperatures, which after cooling formed argentite, tetrahedrite, native silver and electrum in potassic-sericitic zone of porphyry deposits. In this regard, Chaffee [68] reported strong anomaly for silver in potassic-sericitic zone of the Kalamazo porphyry deposit. The Ag/Au ratios in selected Cu-Au porphyry deposits increase with decreasing depth, which may be related to the predominant occurrences of acanthite and electrum toward the shallowest zone of the propylitic and advanced argillic alteration. This is consistent with the Ag/Au ratios and metal zoning around Bingham porphyry systems, as reported by Einaudi [5]. Interestingly enough, Chaffee [68], found high values of silver in the propylitic alteration zone, surrounding the Kalamazo porphyry deposit. Thus, the use of Ag/Au ratios in propylitic alteration zone is the most

Figure 6. Photomicrograph illustrating a) hematite-rich multiphase aqueous, b) a primary polyphase halite-saturated, c) polyphase halite and sylvite saturated aqueous fluid inclusions from the Miocene Gode Kolvary porphyry copper deposit, Iran and d) salinity versus homogenization temperature of the fluid inclusions from the some important Miocene continental arc porphyry copper deposits, Iran.
suitable exploration guide for estimating the vein-type silver-gold mineralization and the proximity to the underlying potassic-phyllitic ore zone. The relationship between (AgxAu)/(CuxMo) ratios and formation depth is significantly better developed in all types of porphyry deposits, as the ratios are meaningfully increased with decreasing depth. Therefore, it is expected that the main Cu-Mo ore body exists at greater depth. This relation is compatible with the suggestions of Beus and Grigorian [48] that higher gold and silver values develop toward the shallowest and at low-temperature zone of porphyry-hydrothermal deposits.

Although alteration and zoning model of porphyry mineralization have been proposed by Sillitoe [21] and Kouzmanov and Pokrovski [65], no model of supra-
ore or sub-ore elemental ratios has yet been suggested. To modelize the elemental ratios, an idealized reconstruction model of porphyry system is revised in Fig. 8. Accordingly, the variations on the \((Ag\times Au)/(Cu\times Mo)\), \(Au/Cu\), \(Cu/Mo\) and \(Ag/Au\) ratios are depicted by vector zoning. This is consistent with the order of elemental halos and alteration zoning of Beus and Grigorian [48]. The illustration shows that the \(Ag/Au\) ratios increase toward the deepest zone of the ore body, whereas the \(Au/Cu\), \(Cu/Mo\)—and \((Ag\times Au)/(Cu\times Mo)\) ratios give an increasing trend toward the surficial part of the porphyry deposit. This increasing trend demonstrates that the main \(Cu\), \(Cu-Mo\) and even \(Cu-Au\) porphyries exist below the supra-ore halos and in the deeper part of the mineralized zone.

**Conclusion**

This investigation highlights that the anomalous supra-ore and sub-ore halos have the potential to assess the relative position of the main porphyry ore zone with respect to the primary hydrothermal halos at different depths or to indicate the exposed level of the mineralized zones.

The increasing trend of \(Au/Cu\) ratios toward the surficial parts of all porphyry deposits might be related to low temperature fluids, bisulfide gold complexes and the presence of bornite or pyrrhotite-rich porphyry and epithermal systems.

The main controlling factors for \(Cu/Mo\) ratios in all porphyry deposits include depth of formation, specific thiomolybdate-sodium complexes, low temperature of hydrothermal fluids, the low concentration of chloride complexes and the high fugacity of \(H_2O\).

The \((Ag\times Au)/(Cu\times Mo)\) ratios reflect a better response to formation depth, hydrothermal zoning and alteration halos than the other elemental ratios and may be used as an exploration guide for all genetic types of the porphyry deposits.

Based on the \((Ag\times Au)/(Cu\times Mo)\) ratio, the \(Cu\), \(Cu-Mo\) and \(Cu-Au\) porphyry deposits formed at <8-0.6 km, <5-2 km and <4-1 km, respectively.

We suggest that the use of \((Ag\times Au)/(Cu\times Mo)\) ratios in drill core samples of any porphyry systems may guide to determine the depth of the main \(Cu-Mo-Au\) mineralized zone or to evaluate the exposed level of many as-yet-undiscovered unexposed porphyry deposits.

Although, the anomalous supra-ore and sub-ore halos in this investigation were developed in hypogene mineralized zones, they are also useful in providing the exploration insights into gossan zones that cap the underlying sulfide enrichment and hypogene zones of the unexposed porphyry deposits.

**Acknowledgements**

I am grateful to Prof. Dr. M R. Nooridaloii, Editor-In-Chief of Journal of Sciences of Islamic Republic of Iran, the Editorial Board and the anonymous reviewers for their professional editorship, regarding the reviewing processes of the manuscript. Also, I appreciate the authors of the several papers, which I have benefited from their knowledge for this paper. I would like to thank the encouraging support of my colleagues at Geological Survey of Kerman, Department of Mining Engineering and Department of Geology of Shahid Bahonar University of Kerman, Kerman, Iran.

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