Gold in the serpentinite weathering cover of the Szklary massif, Fore-Sudetic Block, SW Poland

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Abstract The average gold content in the serpentinite and weathered serpentinite rocks of the Szklary massif (20 samples from the surface and 38 samples from boreholes) is about 4.97 ppb; for the individual rock types: 0.72 ppb for the fresh serpentinite, 3.83 ppb for the weathered serpentinite, and 2.59 ppb for the serpentinite residual soil. The highest gold content was recorded for the talc-rich rocks - 27.84 ppb, while the chalcedony veins accompanying the weathered serpentinite rocks contain 12.03 ppb. The gold distribution in the serpentinite weathering cover has characteristics typical of gold migration in laterite debris. The increased gold content was often associated with the lithological boundaries and with the water-table level. A clear connection with a higher content of other elements, such as Cu, As, Sb, Ni and Zn. However, elevated gold content in the chalcedony veins was not observed to be related to an increase in the amount of chalcopyrite. The native gold in the serpentinite weathering cover usually forms separate irregular blades up to 0.2 mm long, which are isolated or, rarely, associated with oxides (chromite, magnete) and silicates (enstatite, tremolite, anthophyllite). The narrow rims of gold around the rock-forming minerals indicate its secondary nature. The gold bearing phase (Au+Sb+Cu) was also identified, occurring as rare fine grains up to 10 micrometres in length.

INTRODUCTION

The average gold content in the ultramafic rocks is low. The primary gold concentration in the ophiolite complexes does not usually exceed 0.05 ppm (g/t) and often correlates well with the content of platinum group minerals in the rocks (e.g. Basit ophiolite in NW Syria, Trodos ophiolite in Cyprus, Arabian Shield ophiolites - Sharkov et al., 1997; Crocket, 1993).

Increased gold content in ultramafic rocks is generally connected with the activity of hydrothermal solutions, especially where silica-carbonate solutions alter serpentinite. In such cases, the higher gold content is accompanied by higher contents of the chalcopyrite metals (Cu, Ag, Ni, Co). Such gold mineralization is known from, for example, the McLaughlin deposit (Coast Range ophiolite) in northern California (Sherlock & Logan, 1995).

During the serpentinite weathering process, gold remains in native form in the debris, or, when it was associated with minerals, it precipitates and does not migrate far. After the decomposition of gold-bearing sulphides in ultramafic rocks (e.g. pyrite, arsenopyrite, petlandite), distinct concentrations of sometimes form, even when the gold content in the primary minerals was minimal. Gold can be transported and concentrated not only in the form of fine blades and nuggets, but also dissolved in solutions containing the appropriate complexes (HS, Cl, Br, I, \(\text{SO}_4^{2-}\), SCN, CN) and in organic complexes (Seward, 1973; Schenberger & Barnes, 1989, vide Kucha et al., 1995; Samama, 1989). The geochemistry of gold in hypergenic processes depends on the pH and redox potential (\(E_h\)) values of the water environment, and on the presence of complexes in the form of organic and inorganic compounds binding the gold.

Laterite weathering favours gold migration and secondary concentration. It is proven that the gold being dispersed in laterite debris, can subsequently concentrate in zones enriched in Fe and Mn oxides (Flechtinger, 1985 vide Zeegers & Leduc, 1993). An additional factor favouring the high gold concentrations under such conditions is the activity of silica solutions. For example, the gold content in the silicated manganic-ferric ochres of Trodos ophiolite in Cyprus reaches values of 1–5 ppm (Prichard & Maliotis, 1998).

In Poland, gold occurring in serpentinite weathering covers was recorded from the Gogółow–Jordanów massif, connected with the hydrothermal influence of the granite magma of the Strzeżom–Sobótka massif. This activity led to the alteration into talc and chloritisation of the serpentinite and to the formation of quartz veins and microgranite dykes (Fedak & Magdziarz, 1972; Dubińska, 1995; Speczik & Piestrzyński, 1995).
Fig. 1. Sample locations in the Szklary massif (adapted from Niśkiewicz, 1967 and mine maps). Inset map shows the location of the study area in the Bohemian Massif.
The Szklary massif is mainly composed of serpentinite "core" and its metamorphic and mylonitic country rocks (Fig. 1). During the late Tertiary, a thick layer of lat- erite debris formed on these rocks (Niskiewicz, 1967).

The country rocks of the serpentinite are mainly gneisses and amphibolites, among which mylonites and cataclasites occur in the form of small bodies. There are three types of gneisses, forming a significant part of the cover: laminated gneisses, augen gneisses and gneisses lacking distinct orientation. The amphibolites occur as narrow outcrops along the SW boundary of the massif. Niskiewicz (1967) distinguished augen and massive amphi-
bolites.

The serpentinite weathering cover in Szklary developed in situ (Niskiewicz, 1967, and this volume). Weathered serpentinite, but still massive and preserving the original structure, appears at the base of the debris cover just above uncharged serpentinite. Overlying this, there is laterite weathering cover with small blocks of the serpentinite and its accompanying rocks (crushed chaledony veins, vein rocks), with the most disintegrated residual soil on top. Based on the colour and mineral composition of the weathering debris, a few types can be distinguished: brown, green, and cherry-red weathering covers. The most significant portion of the weathering cover is made up of two particular types - brown debris, which has a resid-
ual soil character and dominates in the debris cover, and clayey, grey-green debris which is present in slightly smaller amounts. The green weathering cover is usually richer in Ni, and occurs close to the base of the earthy weathering, just above the massive serpentinite. This type often preserves the primary serpentinite structures and represents the saprolitic zone in the weathering profile of ultramafic rocks, while the brown type usually represents the ochre zone. (Dubinska, 1986; Samama, 1989). An Fe oolite zone, characteristic for a full laterite profile, does not occur in Szklary, although small Fe oolite concentrations, made up of limonite, are present in some of the weathering cover types. Research concerning the amount of platinum group minerals and gold in the serpentinite massif of Lower Silesia has shown that the gold content in the Szklary massif ranges from 0.5 ppb (Niczyprurak, 1997) to 1.2 ppm (Sachanbiński & Lazarienkov, 1994).

Surface samples taken from the closed "Szklary" Mine-Metallurgic Factory, along with samples from drill cores bored in the Szklary massif in the late fifties and early sixties (Niskiewicz, 1967), were used for the research done in 1996-1999. Care was taken to choose the most typical serpentinite weathering covers, as well as samples rocks connected with them i.e.: talc rocks, chlorite-amphibole schists, chaledony veins etc. In total, 58 samples were examined - surface weathering cover samples and samples from two boreholes: Szklary 22 and Szklary 36 (Fig. 1).

The chemical analysis of the content of gold and other metals was performed using two methods: Instrumental Neutron Activation Analysis (FA-INAA) in Activation Laboratory (Ontario, Canada), and the ICP method in Activation Laboratory (Ontario, Canada), and in ACME Analytical Laboratories Ltd. (Vancouver, Canada).

For the ICP method, 1 g samples were dissolved in hot aqua regia and analysed using two kinds of spectrometers: JARELL ASH model Enviro and PERKIN ELMER model 6000. This method guarantees precision to within ±10-20%. The analysis of precious metals using the INAA method was done in NiS alloy, which was prepared from 50g samples. A research reactor 2MW Pool Type (thermal neutron stream 1.0 x 10^11 n cm^-2s^-1), and Ge ORTEC and CANBERRA gamma ray detectors were used for measurements.

Heavy mineral concentrates obtained by gravitational and magnetic separation were used for heavy mineral analysis and searching for gold-bearing phases. The gravitational separation was done both manually, using a gold concentration bowl and a concentration table (Willy type) in the Mine Institute of the Wroclaw University of Technology and via the use of heavy liquid (sodium polytungstate, d = 2.8 g/cm^3) in the Mineral Separation Laboratory of the Institute of Geological Sciences of Wroclaw University. The obtained heavy mineral concentrates were identified using an electron microscope (SEM) with an EDS type microprobe accessory (Jeol JSM-5800LV Oxford) in the Institute of Material Science and Applied Mechanics of the Wroclaw University of Technology.

**CHEMICAL DATA**

Table 1 shows the results of analyses on the content of selected metals, including gold, for 20 weathering cover samples, taken from the surface of closed excavations in central part of the Szklary massif. Gold content analyses were also done for 38 samples coming from the Szklary 22 and Szklary 36 boreholes. Fig. 3 shows the results of gold identification via the FA-INAA method.

A notable feature of the chemical composition of all the types of studied rocks is the elevated amount of nickel, from 0.15 to 1% (the min. average ore content is 0.3 wt % Ni - Niskiewicz & Sachanbiński, 1995). The green weathering cover is characterised by the highest Ni content, along with elevated Cr, Cu and Au contents, while the brown weathering cover has an elevated amount of Ca and Mg. There is a clear connection between the content of gold and of other elements, especially chalcophile met-
als and indicators of gold-bearing mineralization (Cu, Ni, Sb, As, Zn, Ag). The graphs (Fig. 2) present the ratios of
<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample characteristic</th>
<th>Research method</th>
<th>Ni (ppm)</th>
<th>Pb (ppm)</th>
<th>As (ppm)</th>
<th>Sb (ppm)</th>
<th>Fe (%)</th>
<th>Mn (ppm)</th>
<th>Cr (ppm)</th>
<th>Co (ppm)</th>
<th>Cu (ppm)</th>
<th>Ca (%)</th>
<th>Mg (%)</th>
<th>Zn (ppm)</th>
<th>Ag (ppm)</th>
<th>Au (ppm)</th>
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<tbody>
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<td>SK 01</td>
<td>Brown clayey debris with pinemite</td>
<td>ICP</td>
<td>9499</td>
<td>4</td>
<td>186</td>
<td>32</td>
<td>5.16</td>
<td>866</td>
<td>546</td>
<td>91</td>
<td>41</td>
<td>0.29</td>
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<td>93</td>
<td>&lt;0.3</td>
<td>6</td>
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<td>Green-grey, clayey debris, with talc</td>
<td>ICP</td>
<td>10294</td>
<td>5</td>
<td>172</td>
<td>26</td>
<td>4.41</td>
<td>637</td>
<td>449</td>
<td>71</td>
<td>53</td>
<td>0.12</td>
<td>6.39</td>
<td>98</td>
<td>0.3</td>
<td>13</td>
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<td>Green-brown debris with pinemite</td>
<td>ICP</td>
<td>8256</td>
<td>&lt;3</td>
<td>22</td>
<td>29</td>
<td>4.62</td>
<td>787</td>
<td>299</td>
<td>85</td>
<td>16</td>
<td>0.42</td>
<td>9.28</td>
<td>90</td>
<td>&lt;0.3</td>
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<td>Brown debris with magnesite</td>
<td>ICP</td>
<td>2992</td>
<td>&lt;3</td>
<td>17</td>
<td>8</td>
<td>3.82</td>
<td>623</td>
<td>253</td>
<td>73</td>
<td>12</td>
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<td>Brown debris with magnesite</td>
<td>ICP</td>
<td>1922</td>
<td>&lt;3</td>
<td>10</td>
<td>3</td>
<td>4.12</td>
<td>568</td>
<td>160</td>
<td>77</td>
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<td>17.45</td>
<td>34</td>
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<td>1</td>
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<td>Clayey red-brown debris from caprock heap</td>
<td>ICP</td>
<td>3215</td>
<td>&lt;3</td>
<td>6</td>
<td>12</td>
<td>6.63</td>
<td>864</td>
<td>628</td>
<td>14</td>
<td>17</td>
<td>0.12</td>
<td>8.65</td>
<td>67</td>
<td>&lt;0.3</td>
<td>1</td>
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<td>SO 03</td>
<td>Serpentinite debris in Quarternary</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>SZ 01</td>
<td>The most disintegraded soil brown debris</td>
<td>INNA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.5</td>
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<tr>
<td>SZ 06</td>
<td>Talc-chlorite rock</td>
<td>INNA</td>
<td>7060</td>
<td>44</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>1.12</td>
<td>78</td>
<td>50</td>
<td>34</td>
<td>2</td>
<td>0.16</td>
<td>3.22</td>
<td>43</td>
<td>&lt;0.2</td>
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<tr>
<td>SZ 31</td>
<td>Brown debris with magnesite</td>
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<td>-</td>
<td>1.060</td>
<td>1.880</td>
<td>&lt;0.369</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.070</td>
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<td>-</td>
<td>30.60</td>
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<tr>
<td>SZ 32</td>
<td>Green-clayey debris with pinemite</td>
<td>INNA</td>
<td>-</td>
<td>1.870</td>
<td>&lt;1.040</td>
<td>0.300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.940</td>
<td>-</td>
<td>-</td>
<td>31.30</td>
<td>0.038</td>
<td>0.6</td>
</tr>
<tr>
<td>SZ 33</td>
<td>Brown debris with pinemite</td>
<td>INNA</td>
<td>-</td>
<td>0.549</td>
<td>1.140</td>
<td>0.323</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.530</td>
<td>-</td>
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<td>37.20</td>
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<tr>
<td>SZ 34</td>
<td>Brown clayey debris</td>
<td>INNA</td>
<td>-</td>
<td>0.720</td>
<td>&lt;1.040</td>
<td>&lt;0.261</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.700</td>
<td>-</td>
<td>-</td>
<td>81.30</td>
<td>&lt;0.016</td>
<td>&lt;0.5</td>
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<tr>
<td>SZ 35</td>
<td>Weakly disintegraded green clay</td>
<td>INNA</td>
<td>-</td>
<td>2.870</td>
<td>&lt;1.060</td>
<td>&lt;0.264</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.280</td>
<td>-</td>
<td>-</td>
<td>67.00</td>
<td>0.020</td>
<td>0.6</td>
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<tr>
<td>SZ 36</td>
<td>Brown debris with magnesite and chalcedony</td>
<td>INNA</td>
<td>-</td>
<td>&lt;0.267</td>
<td>1.080</td>
<td>&lt;0.267</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.860</td>
<td>-</td>
<td>-</td>
<td>26.80</td>
<td>0.019</td>
<td>&lt;0.5</td>
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<td>SZ 37</td>
<td>Cherry-red debris</td>
<td>INNA</td>
<td>-</td>
<td>&lt;0.256</td>
<td>&lt;1.010</td>
<td>&lt;0.253</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29.600</td>
<td>-</td>
<td>-</td>
<td>134.00</td>
<td>0.029</td>
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<tr>
<td>SZ 41</td>
<td>Chalcedony veins</td>
<td>INNA</td>
<td>-</td>
<td>&lt;0.256</td>
<td>&lt;1.030</td>
<td>&lt;0.256</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.640</td>
<td>-</td>
<td>-</td>
<td>8.07</td>
<td>0.033</td>
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<td>SZ 50</td>
<td>Talc, rusty debris</td>
<td>INNA</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>50.0</td>
<td>-</td>
</tr>
<tr>
<td>SZ 51</td>
<td>Gray weathered serpentine</td>
<td>INNA</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>SZ 53</td>
<td>Talc-clay debris</td>
<td>INNA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>59.0</td>
<td>-</td>
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</tbody>
</table>

The contents of selected elements from several samples from the central part of the Szklary massif (results in Tab. 1). Samples containing an increased amount of gold are characterised by the highest contents of As, Sb, Ni, Zn, and Cu. There is a clear relationship between the occurrence of gold and that of chalcedony-opal veins. In such cases (e.g. sample SZ 41), the higher gold content is not accompanied by an increased amount of As, Sb, Zn and Cu.

The gold content analysis for the particular rock types (Tab. 1, Fig. 3) allows some conclusions to be drawn about the relationship between the gold and those rock types. The highest gold content (50–60 ppb) are associated with the talc rocks, while considerably lower, though still relatively high of around 10–14 ppb are connected with the chalcedony veins.

The maximum amount of Au for the rocks from borehole No 36 (12 and 14 ppb - sample 36/8, from a depth of 16.4 m, and 36/9 from a depth of 17.0 m, both from the weathered, brown serpentinite) is connected with strong silification of the rocks (Fig. 3). The relationship between the gold and chalcedony is also shown by the analyses of samples 36/12 and 36/13 taken from a depth of 22.0 m. Sample 36/12 represents brown serpentinite weathering cover with an average gold content of 0.8 ppb, whereas the gold content of sample 36/13, which is from the white chalcedony vein being in this weather-
Fig. 2. The ratios of metal content in the Szklary weathering covers.

Fig. 3. Gold content in the Szklary 22 and Szklary 36 boreholes.
Fig. 4. The native gold from serpentine weathering crust of the Szklary massif. SEM microphotography (top image). Element distribution maps for O, Si, Au and Cr (four images in the middle), and EDS spectrum of the gold grain (bottom image).

Fig. 5. a. Gold rim around an aluminosilicate grain (BSE image); b. Native gold blades in the heavy mineral suite of the brown weathering cover of the Szklary massif (BSE image).

The highest gold amount in the profile 22 is 10 ppb (sample 22/10 from a depth of 22.5 m) and is also connected with the presence of chalcedony in the weathered serpentine. An increased gold content (6.9 ppb) is at the boundary between brown and green weathering covers (sample 22/6 from a depth of 13.6 m). The occurrence of the highest gold concentration at the roof of the brown serpentine weathering cover is characteristic of both profiles, and is connected with the presence of numerous chalcedony veins. This zone being a lithological boundary, is a kind of geochemical barrier stopping some of the gold migration during the weathering process.

**DISCUSSION AND CONCLUSION**

The profiles of the serpentine weathering cover from the Szklary massif are similar to the general profile of migration and gold concentration in laterite weathering covers described by Zeegers and Leduc (1993). The deep weathering process leads to secondary gold accumulation.
in the oxide zone (the top of the laterite profile) and at the level of the water-table. The Szklary gold, despite occurring in small amounts, behaves in a typical way, during the laterite weathering process, leading to higher gold concentrations at the lithological boundaries, in the zones enriched in Fe and Mn oxides, and the zones with stronger siliceous solutions activity. The most striking feature is the correlation between the gold occurrence and both the talc rocks and chaledony veins.

Fine, a few dozen micrometer long blades of gold were occasionally found during the SEM observation of the heavy mineral concentrates, which were separated from the serpentine weathering cover (Figs. 4 & 5b). In such a form, gold was frequently identified using an electron microscope with EDS system (Fig. 4). Native gold in the form of frayed blades, reaching 0.2 mm in size, were found in the green weathering cover (SK 02) and in the debris of the t alc-chlorite rocks (SZ 06). The presence of native gold as small layers and rims within the rock-forming minerals, which can be observed in a few places, indicates its secondary character (Fig. 5a).

Besides the native gold, individual grains of gold-bearing phases of Au + Sb + Cu composition (EDS analysis Au > Sb > Cu) were observed. Gold generally forms separate grains not associated with the rock-forming minerals. It is sometimes possible to notice a relationship between gold and grains of magnetite and chromite, while connections with silicates (enstatite and tremolite) hardly ever occur.

The average gold concentration in the serpentine weathering cover of Lower Silesia (Niczyperuk, 1997; Sachanbiski & Lazarienkov, 1994; Michalik et al., 1997) is not very high (0.5–10 ppb), and is typical for analogous rocks elsewhere in the world. The gold content in the Szklary serpentine also resembles the average gold concentrations for this type of rocks. The average gold content for all the examined samples is 4.75 ppb, for the fresh serpentine 0.72 ppb, for the weathered serpentine 3.83 ppb, and for the serpentine weathering cover 2.57 ppb (brown type), and 2.67 ppb (green type). The talc rocks, accompanying the serpentine weathering cover, contain the highest average gold content (27.84 ppb). The chaledony veins also usually have an elevated Au content (average 12.03 ppb, Tab. 2). The relatively concentrated gold content in certain profiles and weathering cover types of the Szklary massif is above all a result of the presence of contact zones of the serpentinities and vein rocks. The laterite weathering process also affected the gold distribution in the weathering profile, however zones with increased gold content do not exist here. Gold concentration in some samples is difficult to interpret. Several factors came together to influence the gold distribution in the Szklary massif. They are: varying gold content in the parent rock, migration, secondary concentration during weathering processes, the transformation of serpentine and its weathering cover in contact conditions, and the activity of the cold silica solutions.

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