Physicochemical characteristics and behavior of the serpentinous peridotite outcrops of San Jose and New Idria (California, USA) upon heating treatment

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The iron magnesium ultra basic serpentinous rocks of San Jose and New Idria (California, USA) have been subjected to physicochemical analysis. Changes in the material’s characteristics and behavior as a result of heat treatment have been investigated and quantified by using macro- and microscopic, X-ray and differential thermal analysis. Differences in response to heat treatment were seen for the various samples and could be correlated with the distribution of the ortho- and metasilicate anions participating in the formation of the serpentine silicate lattice (SSL) under hydrothermal conditions. The latter depends on the abundance of the starting minerals in the parent ultra basic rock.

Keywords: serpentinous peridotite, serpentine silicate lattice, silicate anion, Si–O bond

Introduction

Recently a new approach to the thermoacid treatment of serpentinites has opened insights related to the possible use of such rocks [1, 2]. The new approach involves the movement into solution of \((\text{SiO}_4)^{4–}\) orthosilicate anions partitioned from SSL in the form of orthosilicic acid. This has two important implications for serpentinous ultra basic rocks.

First, it provides an avenue that allows one to study and better understand the mechanism and process of serpentine formation under hydrothermal conditions (and some other secondary minerals in our opinion). In other words, it provides an insight into the form and the state of the parent rocks prior to serpentinization. When combined with various physical measurements it provides information about the allocation and the quantity of ortho- and metasilicate anions participating in the formation of the SSL. The latter allows one to differentiate serpentinites according to the character and the behavior of silicate lattice and to try to find an application for serpentinites based on the details of the SSL.

Second, it provides an environmentally friendly, cost-effective, technically achievable, and practical approach for the complex processing of the above-mentioned rocks. This method will allow one to obtain compounds of magnesium and iron with high yields and also light silica and aqua silica gels with unique physicochemical properties [3–7]. Following the aforementioned processing, the residue will be rich in compounds of chrome, cobalt, nickel, etc., which could be extracted with further processing. The quality and quantity of the unreacted residue will be dependent on the properties of the parent rock and its degree of serpentinitization.

On the one hand, the work done will add to the geological knowledge about these rocks, while on the other hand, it will allow selection of the appropriate rock processing parameters for industry.

To date, only a limited number of ultrabasic rocks samples taken from different deposits in Armenia (mainly apodunite serpentines) have been investigated using the thermoacid treatment in conjunction with other physicochemical methods [8]. The results of these investigations have shown that the success of any thermoacid treatment of serpentinites by industry will be highly dependent on the “genetics” of their silicate lattice (SL), while the mineral morphology will play only a minor role [9].

The results of the analogous studies of peridotite serpentinite samples from San Jose (SJ-1, SJ-2) and New Idria (NI-1) (California, USA) deposits are given in this article [10, 11].

The present article reports the results of a physicochemical investigation of the SJ-1, SJ-2 and NI-1 samples. By comparing the results of these new samples with those previously determined for the Armenian samples we will attempt to draw conclusions about the silicon lattice structure based on the quantity and relative concentrations of ortho- and metasilicate anions.

Experimental

Original mineral serpentite from locality San Jose and New Idria (California, USA) was used. The chemical composition of serpentine power was determined by a chemical analysis.
The milling process was carried out in a ball mill with a heat steel chamber. The phase analysis was performed by X-ray diffraction (XRD) with Cu Kα radiation. A Diffractometer Model DRON-3 was used. The differential thermal analysis and thermogravimetric analysis were performed in a MOM Q 1500D derivatograph with a heating rate of 10 °C/min, an air atmosphere, a sample weight of 300 mg and a maximum temperature of 1000 °C.

Results and discussion

The results of chemical analysis of the SJ-1, SJ-2 and NI-1 samples are given in Table 1. As we are primarily interested in the MgO, SiO₂, and volatile content of the rocks, the chemical analysis did not attempt to differentiate the other individual metal oxides, but instead we just give their total amount (R₂O₃).

Table 1. The chemical analysis results of the researched samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Components and their wt. percentage (%)</th>
<th>SUM moles MgO</th>
<th>moles SiO₂</th>
<th>R₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>SJ-1</td>
<td>38.58 SiO₂ 10.93 R₂O₃ 35.72 MgO 14.50 Volatiles 99.73</td>
<td>1.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SJ-2</td>
<td>39.38 SiO₂ 10.06 R₂O₃ 35.97 MgO 14.76 Volatiles 99.67</td>
<td>1.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NI-1</td>
<td>37.11 SiO₂ 13.94 R₂O₃ 34.84 MgO 13.60 Volatiles 99.49</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SH-3*</td>
<td>36.28 SiO₂ 9.51 R₂O₃ 37.37 MgO 14.93 Volatiles 98.09</td>
<td>1.54</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*For comparison, the values for sample SH-3, an Armenian lizardite apodunite [12] with a low antigorite content are given.

Fig. 1. The X-ray powder diffraction patterns of the apoperidotite serpentinites: a– SJ-1, b– SJ-2, c–NI-1. L– lizardite, CCH – clinochrysotile

Visual examination of the samples shows them all to be a fine-grained, compact, schistose mass of the black and green-gray color. Through the microscope the samples clearly appear to be composed of various serpentine minerals with the lizardite variety dominating. All the samples can be considered to be apoperidotite serpentinite.

The XRD analysis of the samples (Fig. 1.) also points to the predominance of lizardite in these samples. In addition the sample SJ-2 contains a tangible amount of clinochrysotile, and the others–mainly orthochrysotile. Lizardite is also partially present in the all paterns.

Fig. 2. Differential thermal curves for the apoperidotite serpentinite samples: a = SJ-1, b– SJ-2, c–NI-1. TG – Thermo gravimetric or weight loss curve, DTG= Differential Thermo gravimetric curve (the derivative of the TG curve), DTA – Differential Thermal Analysis curve. The vertical axis label applies to the DTA curve

Fig. 2. Aperidodites szerpentin minták diff erenciális termikus görbéi: a– SJ-1, b– SJ-2, c–NI-1. TG – termogravimektériás vagy tömegveszteség görbe, DTG – diff erenciális termogravimetricus görbe, DTA – diff erenciális termikus analízis görbe. A függőleges tengely beosztása a DTA görbére vonatkozik.

In spite of the similar SiO₂ and MgO content and overall composition of all the samples, their behavior is different upon heating. As seen in the differential thermal analysis (DTA) curves in Fig. 2. (a, b) for the SJ-1 and SJ-2 samples, intense endothermic and exothermic events occur. However, the curves for the two samples have different peak locations, shapes, and magnitudes. The sample SJ-1 differential thermal analysis (DTA) curve has two maxima (the higher temperature one is observed in the form of a shoulder). The analogous curve for the NI-1 sample differs from the previous ones in having a higher temperature location for the endothermic “peak” and much lower endothermic and exothermic peak intensity.

The X-ray diffraction patterns for the SJ-1, SJ-2 and NI-1 specimens heat-treated at temperatures from 600 °C to 850 °C also have some distinctive features (Fig. 3–5.). For the SJ-1 and SJ-2 samples, the serpentine decomposition starts at lower temperatures than for the NI-1 sample (Fig. 3a; 4a; 5a). Also, the decomposition process for the SJ-1 and SJ-2 samples results in the formation of very little forsterite until temperatures of at least 750 °C. For the NI-1 sample, the forsterite formation begins at the lower temperature where the serpentine decomposition begins.

1 * In Coleman’s commentary all the patterns were characterized in a general way.
By comparing the X-ray diffraction data and the results of the differential thermal analysis of the heat-treated samples we conclude that the endothermic effects curves of the SJ-1 and SJ-2 samples are more intense since they are the result of the two endothermic effects: the removal of constitutional water and the decomposition of most of the SSL, neither of which are not compensated for by the exothermic formation of forsterite and/or enstatite. In this case the recrystallization of the lattice into forsterite does not begin until the SSL is nearly completely broken down. The less intense nature of the analogous curve for the NI-1 sample is likely to be due to the overlap of the two endothermic effects with the exothermic forsterite formation. In fact, for the NI-1 sample, the removal of constitutional water may be accompanied by the nearly simultaneous rearrangement of the SSL into the forsterite lattice.

The results of numerous experiments suggest that in the temperature range of 600–750 °C the formation of forsterite starts in one of two ways. The route chosen depends on the formation of constitutional water and the decomposition of most of the SSL, neither of which are not compensated for by the exothermic formation of forsterite and/or enstatite. In this case the recrystallization of the lattice into forsterite does not begin until the SSL is nearly completely broken down. The less intense nature of the analogous curve for the NI-1 sample is likely to be due to the overlap of the two endothermic effects with the exothermic forsterite formation. In fact, for the NI-1 sample, the removal of constitutional water may be accompanied by the nearly simultaneous rearrangement of the SSL into the forsterite lattice.

The results of numerous experiments suggest that in the temperature range of 600–750 °C the formation of forsterite starts in one of two ways. The route chosen depends on the location of the (SiO₄)⁴⁻ anions. It is the author's opinion that in the formation of forsterite there are the following two routes: the route chosen depends on the determination of the fractional enstatite and forsterite formation. By combining the determination of the fractional enstatite and forsterite formation at temperatures between 600 °C and 850 °C from X-ray diffraction data with the results of the differential thermal analysis (DTA) at temperatures below 850 °C it is possible to determine the number and location of the (SiO₄)⁴⁻ and [(SiO₃)₂⁻]ₙ anions in the SSL.

The above argument is based on the formation of new Si–O bonds that result as the parent silicate rock is transformed into serpentinite under hydrothermal conditions. These newly formed Si–O bonds are thought to be weaker than the standard Si–O and Si–O–Si bonds formed by ortho- and metasilicate anions that remain from the parent material. In other words, during the initial formation of the SSL under hydrothermal conditions at temperature below about 500 °C [13], the newly formed Si–O bonds yield to the original Si–O and Si–O–Si bonds of the parent rock from which the serpentine formed. These leaves isolated tetrahedrons and metasilicate anions in the resulting “lattice” which are only weakly bound because of the absence of full π-bonds that result from the free d-orbital of silicon and the unshared electron pair of oxygen [14].

The above promotes the cutting of the newly formed bonds during heat treatment. Therefore the initial number of the ortho- and metasilicate anions participating in the SSL formation mainly predetermines the quantity of the partitioned versus “free” orthosilicate anions that results from the heat treatment of serpentines. Evidence for this comes from the fact that after thermo acid treatment of the serpentinites which were formed from pyroxenites, the amount of orthosilicic acid released into solution is several times less than that for apodunite serpentinites [9] which were subjected to the same treatment. In other words, for heat-treated serpentines, the combination of the initial temperature of forsterite formation and its dynamics as a function of temperature below 850 °C allows one to determine the approximate proportion and allocation of the ortho- and metasilicate anions that participated in the SSL formation.
Let us now consider several variants of the formation of the SSL and the behavior of the resulting serpentinites upon heating.

1. Apodunite serpentine: in this case great number of \((\text{SiO}_4)^{4-}\) anions must participate in forming the SSL. It is natural to suppose that during the thermal decomposition of this serpentine, the breakdown of the SSL proceeds by rupturing a great number of the new bonds that formed during the serpentine formation. The result is number of \((\text{SiO}_4)^{4-}\) anions that are side-by-side which can immediately form forsterite. However, at temperature below 800 °C the majority of the released \((\text{SiO}_4)^{4-}\) anions remain partitioned. At temperatures above 800 °C these become highly mobile allowing forsterite formation to proceed rapidly. The evidence for this process is the intensive exothermic peak on the DTA curve (Fig. 6.) and in the X-ray powder diffraction patterns (Fig. 7.) of the Sh-3 sample, which is an Armenian lizardite apodunite.

2. Apopyroxenite serpentine: here a great number of \(((\text{SiO}_3)^{2-})_n\) anions participate in the SSL formation. During the thermal decomposition of the SSL these \(((\text{SiO}_3)^{2-})_n\) anions will be released. For this serpentine, the forsterite formation is observed only at temperatures higher than 750 °C and strong endothermic and weak exothermic peaks are seen in the DTA curve. The latter is the result of the formation of both forsterite and enstatite, with the weakness of the exothermic peak being due to the small number of free \((\text{SiO}_4)^{4-}\) anions present. A previous investigation of an apopyroxenite serpentine showed that significant amounts of enstatite are already observed at the temperature of 750 °C in the XRD graphs. It’s clearly seen on the DTA curves (Fig. 8.) and in the X-ray powder diffraction patterns (Fig. 9.) of the Armenian sample 4147B, which is an apopyroxenite serpentine.

3. Apoperidotite serpentine: this form of serpentinite is characterized by a range of behavior which depends on the allocation of the \((\text{SiO}_4)^{4-}\) and \(((\text{SiO}_3)^{2-})_n\) anions participating in the SSL formation and their initial coordination. Let us consider one of the possible variants where we assume we have a comparable quantity of \((\text{SiO}_4)^{4-}\) and \(((\text{SiO}_3)^{2-})_n\) anions participated in the SSL formation. Even here there are at least two different possible behaviors that result from the heating of the serpentine: a) There is an even distribution of the abovementioned anions throughout the SSL: in this case, due to the required migration of the \((\text{SiO}_4)^{4-}\) anions, the forsterite formation only begins at temperatures in excess of 750 °C. The initial stage of the serpentine decomposition is impeded by the shortage of \((\text{SiO}_4)^{4-}\) anions which are located side by side (for example, for the SJ-1 and SJ-2 samples); b) There is an equal allocation but non-uniform distribution of \((\text{SiO}_4)^{4-}\) and \(((\text{SiO}_3)^{2-})_n\) anions: in this case because a considerable quantity of \((\text{SiO}_4)^{4-}\) anions will be located side by side, the exothermic forsterite formation and endothermic SSL decomposition can proceed simultaneously thereby largely compensating one’s heat release by the other’s heat requirement. The result is the observation of a less intense endothermic peak as well as a less intense exothermic peak (for example, for the NI-1 sample). The above effect is also expected to cause the decomposition to begin at lower temperatures. Thus at temperatures higher than 750 °C only a small quantity of \((\text{SiO}_4)^{4-}\) anions is expected to remain, resulting in a smaller exothermic forsterite peak at these higher temperatures. This effect is observed in the DTA curve of Fig. 2. (b).

It should be noted that since both the enstatite and forsterite formation reactions are exothermic, both will contribute to the exothermic peak seen. (On a per gram basis, thermodynamic
data indicate that the exothermicity of forsterite formation is about 1/3 greater than that of enstatite formation.) The existence of both enstatite and forsterite is seen in the XRD analysis of the samples annealed at the temperature 850°C (Fig. 3. (e); Fig. 4. (e); Fig. 5. (e)).

From the above, it is evident that one will only be able to predict the behavior and the ability to potentially utilize a given serpentinite sample by a combination of differential thermal, XRD and chemical analysis.

Conclusions

1. In case of the SJ-1 and SJ-2 heat-treated serpentinite samples, the bulk of the forsterite only begins forming at temperatures above 750°C and this process is being accompanied by a large exothermic peak in the DTA curve.

2. In case of the NI-1 heat-treated serpentinite sample, noticeable amounts of forsterite already appear at a temperature of 650°C and this process is simultaneously accompanied by the SSL decomposition. As a result, the endo- and exothermic peaks in the DTA curve are not very intense.

3. The SJ-1, SJ-2 and NI-1 samples which are all apoperidotite serpentinites are characterized by different behaviors which depend on the relative allocation of ortho- and metasomatic anions and their distribution within the SSL. The samples SJ-1 and SJ-2 SL are characterized by a more uniform distribution of anions than in the NI-1 sample.

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