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# APPLICATION OF THE TPR METHOD FOR THE STUDIES OF Ni(II) IN CHRYSOPRASE

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## Abstract

TPR method was used to elucidate the status of nickel ions in chrysoprase. Temperature profiles of chrysoprase samples were interpreted by comparing them with TPR curves of references. Two kinds of nickel species were identified in the studied samples. The first one is nickel in 2:1 layer silicates while the other is nickel in the extra-framework positions. Apparent activation energies (85±3 and 20±5 kJ mol$^{-1}$) which were obtained from TPR data support the above attribution.

**Keywords:** chrysoprase, nickel locations, thermo-programmed reduction

## Introduction

According to literature most of Ni ions in chrysoprase are present in finely dispersed layer silicates. It was also postulated that Ni ions may occur additionally in the extra-framework positions. Although this suggestion has been presented in the literature over 20 years ago no experimental support was available till now. Our aim was to demonstrate that the Thermo-Programmed Reduction (TPR) method is suitable for providing evidence of the presence of nickel in the extra-framework positions in chrysoprase. Moreover, the use of TPR, which is widely used in chemistry [1], seemed worthy of popularization for mineralogical applications. In the year 2002 it was listed in more than 200 papers, which dealt with characterization of synthetic nickel containing solids and catalysts. In contrast, according to our best knowledge, only one paper which presented TPR investigation performed on mineral samples, was issued before 2004 [2].

## Chrysoprase

Chrysoprase is a complex mineral system composed mostly of a fine-crystalline variety of silica (chalcedony). The characteristic green color of chrysoprase is due to Ni(II) ion content. Chrysoprase was identified for the first time in the 18th century in

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the region of Lower Silesia in Szklary near Ząbkowice Śląskie. The broad review of chrysoprase science, presented by Sachanbiński [3] in 1985, was significantly supplemented during the last two decades by the authors who used different characterization techniques: UV-Vis [4], XRD [5], FT-IR and EPMA [6], TEM [7], EPR and TPR [8]. It is well established [9] that formation of chrysoprase most often occurs upon liquid–solid interactions under ambient conditions.

## Materials

The starting chrysoprase samples referred as Z-5, Z-7 and Z-8 originated from different regions. Z-5 was taken from Szklary (Lower Silesia, Poland), Z-7 from Marlborough Creek (Australia) and Z-8 from Africa (unknown locality). Nickel content in the samples was determined by means of the elemental analysis (Z-5 1.7, Z-7 1.0 and Z-8 4.4 mass% of Ni). The samples were crushed and sieved, only the fraction 0.25–0.3 mm was taken for the TPR experiment.

## Methods

### *TPR*

TPR seems to be an adequate method for investigation of nickel distribution in chrysoprase because different accessibility of hydrogen to sites of various kinds is reflected in the resulting plot. The TPR experiments were carried on 30 mg samples, using a heating rate of 5 K $\text{min}^{-1}$ between room temperature and 1300 K. The flow of gas (5% $H_2$ in Ar, N5 quality, Messer) was set to 6 mL $\text{min}^{-1}$. Evolving water was removed from effluent gas by means of a cold trap. Nickel talc $Ni_3[Si_4O_{10}](OH)_2$ (2:1 layer silicate), nickel lizardite (nepouite) $Ni_6[Si_4O_{10}](OH)_8$ (1:1 layer silicate) and nickel grafted on silica ($Ni/SiO_2$) [9], were used as reference samples for TPR measurements.

### *In-situ XRD*

This method detects structure modifications that accompany the reduction process. In this study experiments were made with the use of X'pert Siemens powder diffractometer equipped with reaction unit. Al-filtered $CuK_\alpha$ radiation was used. Experiments were carried out with 0.3 g samples, gas (5% $H_2$ in Ar) flow-rate was 50 $\text{cm}^3\ \text{min}^{-1}$. XRD measurements were performed at 290, 560, 670, 820, 970 and 1120 K. During aquisition of diffractograms the temperature was constant. Between the temperatures of measurements, the temperature changed at the rate of 5 K $\text{min}^{-1}$.

## Results

### *TPR*

Interpretation of TPR profiles was performed by comparing them with profiles of reference samples and by calculating the apparent activation energies Fig. 1. Two distinct bands are visible on the curve obtained from the investigated sample (curve a). The stronger band lies between 700 and 1100 K (region 2) and corresponds to the reduction curve of Ni(II) in layer silicates of 2:1 type which is represented here by Ni-talc (curve b). The weak and wide low temperature band which appears in region 1 (400–700 K) matches to the profile of isolated (extra-framework) nickel ions grafted on the surface of silica gel during reduction (curve d). The described experiment gave no evidence for the presence of Ni containing 1:1 layer silicates (curve c).

Apparent activation energies were obtained from TPR data Fig. 2. Activation energy calculated from the low temperature part is equal to 20±5 kJ $\text{mol}^{-1}$ while the one taken from the high temperature part is 85±3 kJ $\text{mol}^{-1}$.

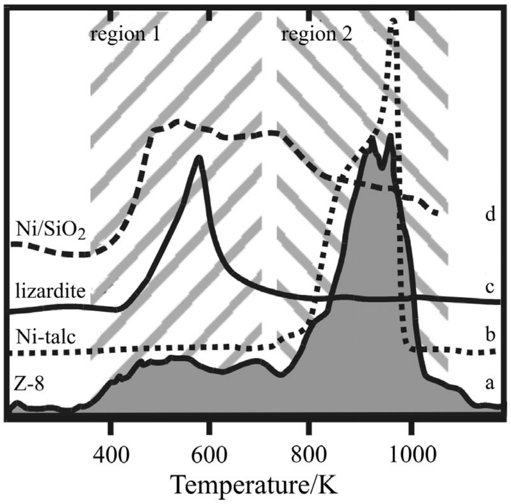

**Fig. 1** TPR profiles of a – the investigated African chrysoprase Z-8 and b – references: Ni-talc, c – Ni-lizardite and d – $Ni/SiO_2$

### *In-situ XRD*

The high-temperature TPR peak of the chrysoprase was attributed to 2:1 nickel phyllosilicates [8]. In spite of the fact that thermal methods are very sensitive for subtle structural properties and their changes [10], we tried to find the independent proof for the above attribution because small amounts of contaminating anions strongly change the reducibility of nickel species [11] and may cause the interpretation of TPR curves ambiguous. Hence, we performed an XRD experiment, in which samples were reduced under the same conditions as earlier in TPR experiments. Reduction of nickel phyllosilicates leads to destruction of their structure [11] and change of their lattice parameters. Assuming that the high-temperature TPR peak is due to 2:1 phyllosilicates, one should observe a significant drop of the XRD intensity of (001) phyllosilicate peak at the range of high-temperature peak. However, (001) should be unaffected in lower temperatures.

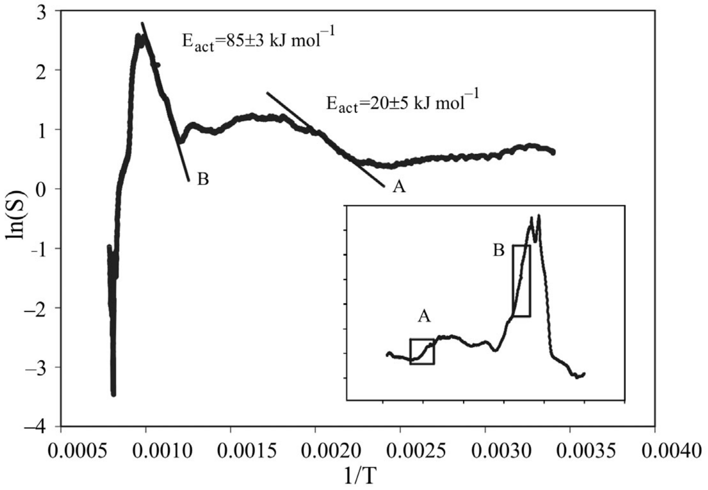

**Fig. 2** The original (*S vs. T*) TPR curve of Z-8 sample (inset) and transformed to Arrhenius plot (ln(*S*) *vs.* 1/*T*). Activation energy was determined for regions A and B

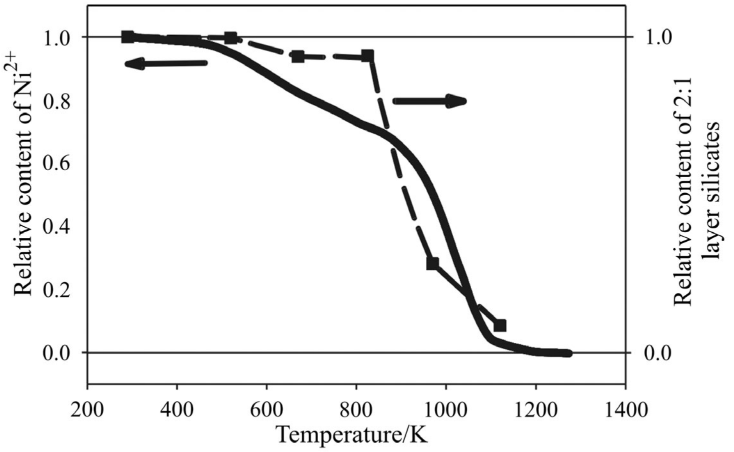

**Fig. 3** Comparison of the relative $Ni^{2+}$ content (solid line) calculated from TPR profile and the relative content of 2:1 layer silicates (dashed line) obtained from XRD experiment

The results are presented in Fig. 3. In fact a significant correlation between TPR and XRD intensities is observed at the range of high-temperature reduction peak. Moreover, diffraction patterns show the absence of 0.7 nm peak, which should be observed in the presence of 1:1 phyllosilicates.

## Discussion

The origin of chrysoprase influences its later transformations. Chrysoprases are formed in consequence of weathering of ultramafic rocks [3]. During this process, which usually runs at ambient conditions, rocks are periodically penetrated by water solutions. Silica and nickel ions are gradually washed out from mother rock and transported away. Silica and nickel may precipitate together, giving rise to a chrysoprase, which is composed of ca. 98–99 atomic% of $SiO_2$ and 0.5–2 atomic% of nickel ions typically. Nickel ions do not accept tetrahedral configuration and hence cannot replace Si in silica [12]. As a result of this restriction silica tends to form nickel free grains, which initially are very small. Nickel complexes may either agglomerate to bulk nickel oxide/hydroxide or may form surface nickel phase. Investigation of thermal effects associated with the incorporation of nickel complexes into bentonites [13] points at the possibility of imperfect chlorite-like structure formation. Various authors [6, 7, 10, 14] reported the formation of surface nickel phase, while, the presence of the bulk nickel oxide was excluded [4]. A high degree of dispersion of silica and nickel moieties at the initial state of chrysoprase formation suggests that chrysoprase is thermodynamically metastable. If so, it should undergo slow evolution toward minimum of their thermodynamic potential, which agrees with the observation of Kermarec and Che [10]. Depending on the availability of penetrating water, surface nickel phase and silica partially dissolve according to the following reactions and react together [15]. In the equations below some water molecules are omitted for clarity:

$$Ni^{2+}OH_2+OH^{-}\rightarrow Ni^{+}OH+H_2O \tag{1}$$

$$Ni^{+}OH+SiOH\rightarrow SiONi^{+}OH_2 \tag{2}$$

$$SiONi^{+}OH_2+OH^{-}\rightarrow SiONiOH+H_2O \tag{3}$$

$$SiONiOH+SiOH\rightarrow SiONiOSi+H_2O \tag{4}$$

Products of the reactions 2,3 and 4 (Si/Ni dimers and Si/Ni/Si trimers) are considered to be key building blocks of nickel layer silicates (1:1 and 2:1, respectively) [15]. Such low oligomers belong to the broad category of 'extra-framework nickel ions'. Formation of layer silicates stops when the concentration of individual building blocks drops. As a consequence, some nickel ions should always be present in extra-framework positions. Thermodynamics favors the formation of 2:1 layer silicates [16], so the 1:1 silicates disappear gradually, and the presence of these silicates allows for labeling the chrysoprase as relatively 'young'.

Apparent activation energies calculated from the experimental data were compared with the data, which are available from the literature. No direct measurements of activation energy of chrysoprase were reported, hence, the values for similar systems were used for interpretation. The value of $85\pm3$ kJ $mol^{-1}$ which was obtained from the high-temperature part is almost identical as 85.4 kJ $mol^{-1}$ that was reported for nano-agglomerate NiO (surface) reduction, while diffusion controlled bulk reduction of NiO gives 105.1 kJ $mol^{-1}$ [17]. It seems that reduction of nickel that is present inside layer silicates is similar to surface NiO reduction process. The second value of activation energy (20±5 kJ $mol^{-1}$) taken from the low-temperature (extra-framework) region is more ambiguous. It is below all the activation energy values which were found for solid Ni–O systems, and can only be roughly compared to $\Delta_r G^0$ of the reaction $Ni^{2+}+2e^- \leftrightarrow Ni$ (24.8 kJ $mol^{-1}$) [18] in liquid phase. As we know that the extra-framework nickel ions are low oligomers and individual ions, the above comparison seems to be allowed in the first approximation.

## Conclusions

The experiments carried out by means of TPR showed that:

- No Ni-lizardite (1:1 silicate) peak is present in the TPR curve of the studied samples.
- Extra-framework (grafted) nickel was ascribed to the low temperature part of chrysoprase TPR profile.
- The majority of $Ni^{2+}$ ions in all the investigated samples is reduced at temperatures similar to those of Ni-talc (2:1 silicate) reference.

In situ XRD experiments pointed at:

- The absence 001 reflection of 1:1 silicate in our samples. This result means that all the samples are close to thermodynamic equilibrium.
- The disappearance of 001 reflection of 2:1 silicate peak at the temperature of the main TPR reduction peak. It proves that high-temperature part of the TPR profile was properly interpreted.

All the above data show that TPR method may be very useful in solving some mineralogical problems.

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