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OXYGEN ISOTOPE EVIDENCE FOR LOW TEMPERATURE FORMATION OF CHRYSOPRASE.

Chrysoprase is a green colour mixture (variety) of cryptocrystalline or amorphous silica (usually opal and chalcedony phases). Only two locations of chrysoprase are currently known in Europe. Both of them are in SE Poland namely Szklary and Wiry mines. The origin of this variety of silica has been discussed for more than 200 years. The most important discussed factors are the temperature and origin of the solutions responsible for formation of the chrysoprase.

MATERIALS AND METHODS

About 20 mg of powder have been drilled out from each sample of chrysoprase. CO₂-laser ablation preparation technique has been applied for oxygen isotope analysis. Each sample has been prepared and analysed twice. The obtained CO₂ was then introduced to mass spectrometer (Varian Mat CH7) and the oxygen stable isotope ratio ($\delta^{18}\text{O}$) was measured (with precision $\pm 0.05\text{‰}$). Values are quoted relative to SMOW with precision $\pm 0.35\text{‰}$ (Jędrysek and Weber-Weller 2000, Skrzypek *et al.* 2001).

RESULTS

The $\delta^{18}\text{O}$ value in the chrysoprase of pure gemmological value, ranges from 24.88‰ to 32.74‰ (Szklary); from 23.60‰ to 31.04‰ (Wiry), from 27.18‰ to 28.71‰ (Marlborough Creek, Australia), and 25.17‰ (Sarykul Boldy, Kazakhstan). The $\delta^{18}\text{O}$ value of all chrysoprase samples analysed ranges from 22.03‰ to 32.74‰ (with mean average 26.03‰). Remarkably, the $\delta^{18}\text{O}$ value does not correspond to mineralogical variability observed (*e.g.* chalcedony/opal ratio) nor geological position of the chrysoprase analysed. This suggests that the mechanism of chrysoprase formation is uniform with respect to temperature, origin of water and water-to-rock ratio. High oxygen isotope ratios evidence that the chrysoprase precipitated from mixed solution of meteoric at pneumo-hydrothermal

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conditions. This is consistent with fluid inclusion results (Kozłowski and Sachanbiński *et. al.* 1984). Nevertheless, in this study, $\delta^{18}\text{O}$ -based (oxygen isotope fractionation in chrysoprase-water system) paleotermometric estimations are rather of qualitative than quantitative value. This is due to the fact that, in this study, we do not have reliable mineral-mineral oxygen isotope pair. Extensive isotope and mineralogical studies (Jędrysek and Sachanbiński 1994) evidence that chrysoprase-host serpentinite rocks, were changed (weathered) at warm climate. Thus, we accepted, to our calculations, that the $\delta^{18}\text{O}$ value of water, present during formation of chrysoprase, was not lower than -8‰ but not higher than 4‰ . Likewise, the lowermost $\delta^{18}\text{O}$ value of chrysoprase analysed was 21‰ (mean 24‰) and the highest $\delta^{18}\text{O}$ value was 29.4‰ . The other isotope pair has been calculated for magnesite-water and silica-water systems due to Zheng (1999), and Kita *et. al.* (1985) equations (see Fig. 1.).

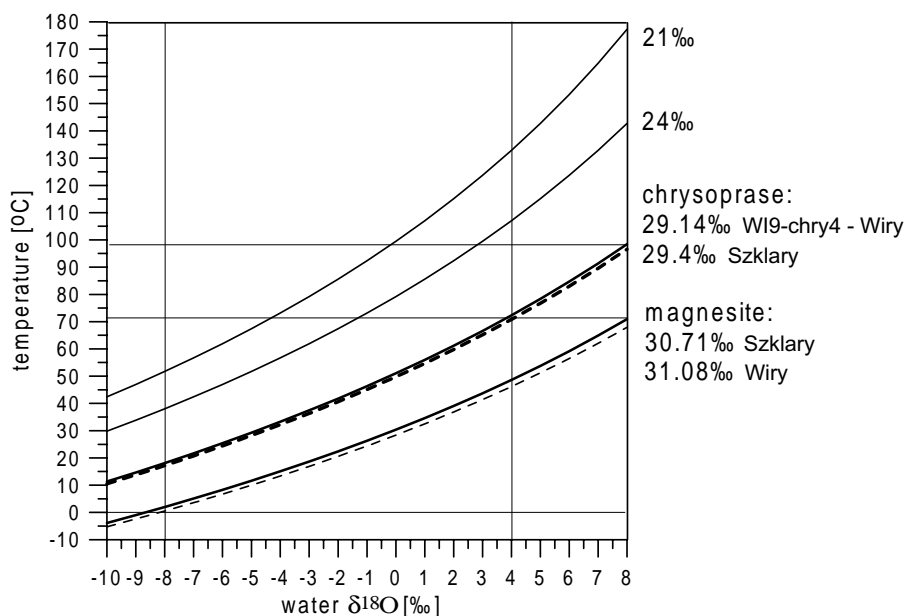


Figure 1. The calculated range of temperature of chrysoprase and magnesite formation. These curves have been calculated due to Zheng (1999) and Kita *et al.* (1985) equations.

It was concluded that the $\delta^{18}\text{O}$ values of magnesite are apparently not syngenetic to chrysoprase. For magnesite following $\delta^{18}\text{O}$ values were found 30.71‰ (Szklary) and 31.08‰ (Wiry) (Jędrysek and Sachanbiński 1994) whereas the $\delta^{18}\text{O}$ values of chrysoprase were 29.40‰ and 29.14‰ respectively.

CONCLUSIONS

1. The following temperatures of crystallisation of chrysoprase (under oxygen isotope equilibrium with $\delta^{18}\text{O}$ of water range from -8 to $+4\text{‰}$) have been calculated: from $5\text{-}55^\circ\text{C}$ to $40\text{-}115^\circ\text{C}$ (Szklary); from $10\text{-}60^\circ\text{C}$ to $40\text{-}110^\circ\text{C}$ (Wiry); from $20\text{-}75^\circ\text{C}$ to $25\text{-}85^\circ\text{C}$ (Marlborough Creek) and $30\text{-}95^\circ\text{C}$ (Sarykul Boldy). Summing up, the estimated isotope temperature of crystallisation of chrysoprases ranges from 5 and 132°C . Therefore, it is in general higher than that of vein magnesite (the maximum range $0\text{-}47^\circ\text{C}$).
2. Diverted crystallisation temperatures and $\delta^{18}\text{O}$ values of chrysoprase and magnesite, evidence oxygen isotope disequilibrium in the chrysoprase-magnesite system, thus suggest that these minerals are not of syngenetic origin. They probably crystallised independently during subsequent stages in evolution of ultramafic rocks. Magnesite have been probably formed in the later stage, following chrysoprase formation.
3. Chrysoprase from Poland, Kazakhstan and Australia probably precipitated from warm solutions at similar conditions.

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