Mineralogical-petrological and experimental investigations of pyrometamorphic rocks from the Hatrurim Formation (Israel)

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The aim of the investigation was the mineralogical and petrological description of pyrometamorphic rocks from the Hatrurim Formation combined with experimental investigations and pseudosection modelling. The rocks from the Hatrurim were formed by combustion pyrometamorphism of limestones and marls. They contain several unusual minerals, like nagelschmidtite and brownmillerite, kalsilite-O1 (monoclinic polymorph) which are to date only known from synthetic cement clinkers. The analyzed rocks from the Hatrurim contain a complex mineral assemblage of gehlenite, kalsilite-O1, pseudowollastonite, Ti-garnet, apatite, rankinite und hematite and the thermodynamic calculations indicate extremely high temperatures >1200°C. Five experiments using natural dolomites and quartzphyllite starting materials were carried out at temperatures of 1200°C and 1300°C. The mineralogical comparison between the natural samples and the experiments showed only agreement concerning a few minerals, such as gehlenite and garnet.

Characterization of Ti-bearing garnets from the Hatrurim Formation (Israel) was realized through the utilization of optical microscopy, µ-XRF (micro-X-ray fluorescence) spectroscopy, EMPA (electron microprobe analysis), Raman spectroscopy and SCXRD (Single Crystal X-Ray Diffraction) on the sample Apo4. The main paragenesis was identified as Ti-garnet, kalsilite-O1, apatite, rankinite, wollastonite and gehlenite. Further identified minerals are flamite, barioferrite, magnetite and a mix of (Ni,Cu)-spinels. Distinctive color zoning, observed in Ti-garnets, was analyzed with all methods, mentioned above. The measured TiO_2 concentration (from 2 to 13 w%) and SiO_2 (from 25 to 34 w%) in Ti-garnets are highly correlated. Mineral formula calculations of garnet yielded the garnet endmembers andradite, schorlomite-Al, schorlomite and grossular in accordance with the observed Ti-zoning. These results helped to derive the possible cation exchange mechanisms $Ti^{4+} \rightarrow Si^{4+}$ trough displacement of Al^{3+} or Fe^{3+} from the octahedral position to the tetrahedral position, or the direct exchange of [r + OH_4] 4- → Si^{4+}. Raman spectroscopy supports these estimations through displacement of the tetrahedral vibration bands to lower wavenumbers. Raman measurements also provide evidence of an OH component on the tetrahedral position, which is obviously independent of the Ti-concentration. The unit cell parameters of garnet crystals with different Ti content (TiO_2≈ 2-13 wt%), and other minerals were determined using single-crystal X-Ray diffraction method. The crystal structure characterization of Ti-bearing garnets was done applying site population refinements. Results of refinement have confirmed that these Ti-garnets are characterized by the schorlomite substitution $Ti^{4+} \rightarrow Si^{4+}$, where Ti^{4+} preferentially occupies the octahedral (Y) site and mainly Fe^{3+} occupies the tetrahedral (Z) vacancies. Furthermore, unit cell parameters and refined chemical compositions of garnets with different Ti content can be directly compared with crystal-chemical analysis of Ti-bearing andradites from different localities in the world (Armbruster et al. 1998).

Thermodynamic calculations using the software THERMOCALC only yielded limiting T-estimates between 1136°C and 1500°C. Pseudosection calculations using the software DOMINO yielded a narrow range of temperatures between 1120° and 1250°C.