

s5.m15.p6 **Microstructure of chert as shown by TEM. I.** Dódony<sup>a,b</sup>, V. Kovács Kis<sup>a</sup> and P.R. Buseck<sup>b,c</sup>, <sup>a</sup>Department of Mineralogy, Eötvös Loránd University, H-1117, Budapest, Pázmány Péter sétány 1/c, Hungary; <sup>b</sup>Department of Geological Sciences and <sup>c</sup>Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, USA. E-mail: vis@ludens.elte.hu

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Moganite was introduced as a new silica polymorph in the eighties [1]. Its structure was described as periodically Brazil-twinning low-quartz [2], in which the thickness of twin lamellae are equal to the value of quartz  $d_{(101)}$ . Moganite proved to be widespread, and XRD patterns of bulk microcrystalline silica are interpreted as an intergrowths of quartz and moganite [e.g. 3].

TEM images of a microcrystalline quartz typically show planar defects, and their SAED patterns are streaked and contain extra reflections. These defects are interpreted on the basis of Brazil-twins as moganite units. However, the observed non quartz reflections are either forbidden in the moganite structure (Sg:  $I2/a$ ) or are more intense than predicted by calculations. Additionally, streaking and rows of extra reflections parallel to  $\langle 011 \rangle^*$  quartz are evident in published SAED patterns of microcrystalline silica [4]. Since  $\langle 101 \rangle$  and  $\langle 011 \rangle$  are nonequivalent in the quartz structure the twinning along these directions must be different. Although these inconsistencies were mentioned by Heaney et al. [4] and Xu et al. [5], the details of  $\{101\}$  and  $\{011\}$  Brazil twinning in quartz-moganite relation is still an open question.

The fibrous appearance and microstructures in moganite-quartz system are interpreted as the result of closely spaced twins. Spiral growth produced by screw dislocations and a self-organizational model were proposed as consistent with the fibrous structure and as possible operating mechanisms. Cady et al. [6] pointed out that these models do not provide a satisfactory explanation of the observed planar disorder.

We report the results of TEM and SAED investigations on chert, a microcrystalline variety of silica. Contrary to studies that focused on the fibrous component, we examined an equigranular microcrystalline silica. We show that the defect structure is independent of the fibrous texture and that the alternation of the right and left quartz lamellae may be random or periodic over a large area, forming intimate intergrowths of quartz lamellae resulting different structure along  $\langle 101 \rangle$  and  $\langle 011 \rangle$ . We present SAED patterns and high-resolution images of chert and interpret the structural data relative to models that involve a moganite component.

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s5.m15.p7 **Structural behaviour of a Mg-hercynite crystal under oxidation.** Lavina B.<sup>a</sup>, Princivale F.<sup>b</sup>, Della Giusta A.<sup>a</sup>, <sup>a</sup> Dip. Mineralogia e Petrologia, Univ. Padova, <sup>b</sup>Dip. Scienze della Terra Univ. Trieste, Italy. E-mail: barbara.lavina@poste.it

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One synthetic single crystal of Mg-hercynite ( $\text{Fe}^{2+}_{0.699}\text{Mg}_{0.301}\text{Al}_{1.941}\text{Fe}^{3+}_{0.059}\text{O}_4$ ) was progressively oxidised in order to investigate structural changes occurring during the formation of a non-stoichiometric phase, from such an important composition for Earth Sciences.

Annealing at 500°C (from 24 to 212 hours) produced only slight changes in structural parameters but a substantial decrease in refinement disagreement factors. Great transformations occurred after annealing at 600°C (from 24 to 1640 hours), showing nearly logarithmic dependence on time. Cell edges, oxygen positional parameters, and mean atomic numbers (man) in T site decreased respectively from 8.14 to 8.10 Å, 0.263 to 0.261, and 21.0 to 18.9. No deviations from Fd3m symmetry were detected. The displacement parameters of O and M sites greatly increased with annealing (from 0.004 to 0.007 Å<sup>2</sup>, and 0.009 to 0.12 Å<sup>2</sup>, respectively), suggesting increasing configurational disorder in these two sites. Otherwise, the T site thermal parameter showed only a small increase after the first runs, and then remained almost unchanged. Related to this increase in displacement parameters was the progressive loss of observed reflections (from 150 to 130), due to a decrease in intensity under the limit of  $4\sigma(I)$ . Oxidation of the crystal proceeded with the absorption at the surface (increasing its volume) of oxygen, ionised by  $\text{Fe}^{2+}$  oxidation to  $\text{Fe}^{3+}$ , and the formation of a defect crystal structure by cation diffusion from inside the crystal towards the new added cells. The hercynite component of the crystal was transformed into a solid solution, given by  $2/3 \gamma\text{-Al}_2\text{O}_3$  and  $1/3$  maghemite ( $\text{Fe}^{3+}_{8/3}\text{O}_4$ ). This solid solution had smaller cell edge and man per formula unit, consistent with observed changes.

At the end of the experiment 0.19 afu of  $\text{Fe}^{2+}$  remained; 71% of the original  $\text{Fe}^{2+}$  had been transformed into  $\text{Fe}^{3+}$ .

Cation distribution between the tetrahedral and octahedral sites was evaluated on the basis of observed bond distances and site electrons. Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  showed tetrahedral site preference. The formal charge on T site showed a progressive increase with oxidation, whereas that of M site decreased. Bond valence calculations showed a progressive increase in the differences between site charges and bond valence sums, so that strain increases and the structure becomes progressively less stable.