

**On the nature of Guinier-Preston zones in meteoritic and lunar orthopyroxene** F. Langenhorst<sup>1</sup>, J.R. Smyth<sup>2</sup>, and H. Kroll<sup>3</sup> <sup>1</sup>Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Burgweg 11, D-07749 Jena, Germany; Falko.Langenhorst@uni-jena.de, <sup>2</sup>Department of Geological Sciences, University of Colorado, Boulder, CO 80309, USA; Joseph.Smyth@colorado.edu, <sup>3</sup>Institut für Mineralogie, Westfälische Wilhelms-Universität Münster, Corrensstraße 24, D-48149 Münster, Germany.

**Introduction:** Upon cooling in their host rocks, orthopyroxenes undergo cation ordering and exsolution processes. The state of order achieved during cooling [1] and the type and morphology of the exsolution products depend on the rate of cooling. Often, the formation of stable exsolution phases is preceded by the formation of metastable phases, e.g. Guinier-Preston (GP) zones. GP zones consist of disc-shaped platelets which are coherently intergrown with the orthopyroxene host, oriented parallel to (100), only one to a few unit cells wide. They are enriched in Ca but differ structurally from monoclinic clinopyroxene [2-5]. In a previous model [3], GP zones being several unit cells wide were interpreted to possess  $Pbc2_1$  symmetry and to consist of two half-unit cell layers with Wo0 and Wo50 compositions. This model assumes that the Ca cations have completely ordered in one half-unit layer of 9 Å width.

**Methods and motivation:** We have readdressed the question of the structure of GP zones, using transmission electron microscopy (TEM). The TEM observations were performed on orthopyroxene from the Johnstown achondrite and a lunar troctolite (76535) [3, 4]. Energy-dispersive X-ray analyses recorded on the TEM confirm the enhanced Ca content within the zones. However, a quantitative determination of the Ca content across the GP zones is presently almost impossible due to their small size. The Johnstown orthopyroxene contains GP zones apparently one single unit cell in width (18 Å), whereas the lunar orthopyroxene is penetrated by GP zones up to three unit cells in width.

To better constrain the structure of the GP zones we used selected area electron diffraction and high-resolution TEM combined with numerical simulation. To determine the space group symmetry of GP zones and orthopyroxene hosts, the electron diffraction patterns have been taken along the crystallographic  $a$ ,  $b$  and  $c$  axes.

**Results and discussion:** *Electron diffraction.* The diffraction patterns of Johnstown and lunar host orthopyroxenes show absences of reflections that are characteristic of the space group  $Pbca$ . This is the space group expected for orthopyroxene.

However, the electron diffraction patterns taken from host regions containing GP zones reveal a reduction in symmetry. In case of the Johnstown orthopyroxene, which contains GP zones of only one single unit cell in width, the  $(hk0)$  electron diffraction pattern taken along the  $c$ -axis shows streaks along the  $a^*$ -axis (inset in Fig. 1), possibly indicating violation of the  $a$ -glide parallel to (001). In the  $(0kl)$  diffraction pattern of the GP zones, the even and odd  $0k0$  reflections are both present. The preservation of odd reflections cannot be explained by double diffraction and thus indicates violation of the  $b$ -glide parallel to (100). The  $(h0l)$  diffraction pattern shows the absence of odd  $00l$  reflections, which is due to  $c$ -glide on the (010) plane.

Except for  $(hk0)$ , similar diffraction patterns are obtained from GP zones in the lunar orthopyroxene. Here, elongated odd  $h00$  reflections in the  $(hk0)$  pattern demonstrate clear violation of the  $a$ -glide (inset in Fig. 2). This observation confirms previous TEM results, obtained on the same lunar sample [3].

Altogether, the diffraction data point to a space group of GP zones that has a lower symmetry than the previously suggested space group  $Pbc2_1$ [3]. The violation of  $a$ - and  $b$ -glide is compatible with the monoclinic space group  $P2_1/c$  that has been proposed by [6].

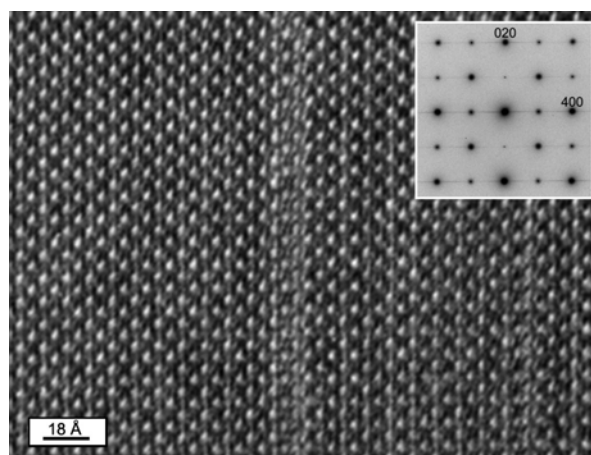


Fig. 1.  $(hk0)$  high-resolution TEM image of Johnstown orthopyroxene with a Guinier-Preston zone. Inset shows the corresponding selected area electron diffraction pattern.

*High-resolution transmission electron microscopy:*

High resolution images taken along the  $c$ -axis of Johnstown (Fig. 1) and lunar orthopyroxene (Fig. 2), i.e. in the direction of chains of  $\text{SiO}_4$  tetrahedra, show that the GP zones are fully coherent with the orthopyroxene lattice.

In Johnstown orthopyroxene the GP zones are in fact thinner than a single  $18 \text{ \AA}$  layer (Fig. 1). This observation supports that Ca is concentrated within (100) sublayers of the unit cell. Numerical simulations of HRTEM images have been performed to test this hypothesis, employing various models for the distribution of Ca. These simulations confirm that enrichment of Ca in a coherent  $9 \text{ \AA}$  layer would result in an enhanced intensity in HRTEM images.

To tackle the question of Ca ordering within alternating  $9 \text{ \AA}$  layers [2], HRTEM observations on the lunar orthopyroxene were required because here the lenticularly shaped GP zones are up to  $54 \text{ \AA}$  thick (Fig. 2). The images show a clearly visible (100) lattice repeat of  $18 \text{ \AA}$ , supporting the view of a violated  $a$ -glide. Within a unit cell layer we do, however, not observe a variation of intensity, suggesting that Ca is likely to be homogeneously distributed within the GP zones.

**Conclusions.** TEM analysis shows that the GP zones are metrically orthorhombic but possess monoclinic symmetry. The enrichment of Ca within GP layers in orthopyroxene causes an asymmetric distortion of the lattice of the orthopyroxene host and a local reduction of symmetry, which is consistent with the previously suggested  $P2_1/c$  space group [6]. The HRTEM observations combined with numerical simulations suggest that there is no ordering of Ca within (100) sublayers of the unit cell.

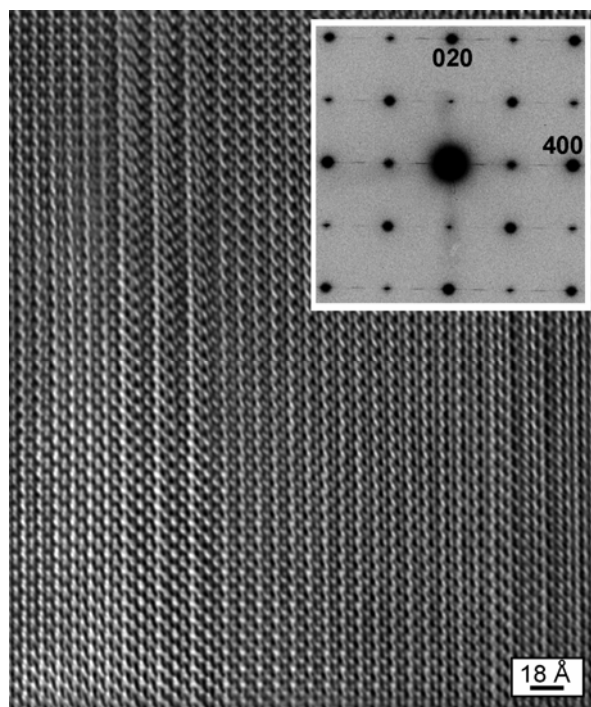


Fig. 2. ( $hk0$ ) high-resolution TEM image of orthopyroxene from lunar troctolite 76535 containing Guinier-Preston zones. Inset shows the corresponding selected area electron diffraction pattern.

**References:** [1] Kroll H. (2003) *Eur. J. Min.*, 15, 7-19. [2] Champness P.E. and Lorimer G.W. (1974) *Phil. Mag.*, 30, 357-365. [3] Nord G.L. (1980) *Phys. Chem. Min.*, 6, 109-128. [4] Heinemann R., Kroll H., Langenhorst F., Lueder T. (2000) *Eur. J. Mineral.*, 12, 163-176. [5] Cámara F., Doukhan J.-C., Domeneghetti M.C., Zema M. (2000) *Eur. J. Mineral.*, 12, 735-748. [6] Smyth J.R. and Swope R.J. (1990) *Phys. Chem. Min.*, 17, 438-443.

**Acknowledgments:** We are grateful for the financial support provided by the Deutsche Forschungsgemeinschaft (DFG grants LA 830/5-1,2; KR 768/18-1,2).