Microtextures and crystal chemistry of pigeonite in the ureilites
ALHA77257, RKPA80239, Y-791538, and ALHA81101

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Abstract—The microtextures of pigeonite in four ureilites, Allan Hills (ALH) 77257, Reckling Peak (RKP) A80239, Yamato (Y-) 791538, and Allan Hills A81101, chosen to span a range of composition and shock level, were investigated by transmission electron microscopy (TEM); two of the samples were also investigated by single crystal X-ray diffraction to determine Fe$^{2+}$-Mg cation site partitioning.

The low-shock and compositionally homogeneous pigeonites in ALHA77257 and RKPA80329 (Wo 6.4 for both, mg 86.3 and 84.3 respectively) display irregularly spaced, shock-induced stacking faults oriented parallel to (100), and large antiphase domains (50–100 nm). Antiphase domains have no preferential orientation. No evidence of exsolution was observed.

The low-shock Y-791538 pigeonite is homogeneous and has higher Ca and mg (Wo 9.4, mg 91.2). TEM investigation showed spinodal decomposition, indicative of incipient exsolution; small antiphase domains were observed ($\approx$ 5 nm). Single crystal refinement yielded $R_{\text{meas}} = 5.71\%$, with Fe$^{2+}$-Mg partitioning coefficient $k_D = 0.077(8)$ and $T_c = 658(35)$ °C.

ALHA81101 has compositionally heterogeneous pyroxenes, with large local variations in Wo and mg (Wo = 4–13, mg = 86–68). No compositional gradients from core to rim of grains were observed, and the heterogeneity is interpreted as related to cation migration during shock. In one relatively Ca-rich region (Wo $\approx$ 12), TEM analysis showed augite-pigeonite exsolution lamellae, with spacing 145(20) nm.

Results for ALHA77257, RKPA80239, and Y-791538 support a model of rapid cooling following breakup of the ureilite parent body. The presence of exsolution lamellae in ALHA81101 can be related to a local shock-induced Ca enrichment and provides no constraint on the late cooling history.

INTRODUCTION

The analysis of microtextures in minerals via transmission electron microscopy (TEM) is a powerful technique for constraining the thermal and shock history of a meteorite. Such analysis relies upon the correlation of microtextures with experimental or theoretical data, on temperature and pressure conditions of formation, and on the kinetics of their formation. Pyroxenes are especially suited for such an investigation because 1) exsolution textures, antiphase domains, and microtwinning are commonly present; 2) a number of theoretical and experimental investigations have been performed on pyroxenes to constrain the observed textures; and 3) pyroxenes are ubiquitous in several meteorite groups, which allows interesting comparative studies.

Among pyroxenes the Ca-poor monoclinic $P2_1/c$ pigeonite is of specific interest. Pigeonite is invariably formed at high temperature and during cooling enters the orthoclinopyroxene two-phase field. Therefore, pigeonite can be homogeneous at the atomic scale only after very rapid cooling. Very slow cooling results in complete inversion to orthopyroxene and exsolved clinopyroxene. Furthermore, there is a series of intermediate microtextures between homogeneous pigeonite and exsolved orthopyroxene, which can be related to the cooling rate.

Microtextural data can be supplemented by single crystal X-ray diffraction data (XRD) to retrieve Fe$^{2+}$-Mg intracrystalline partitioning between the M1 and M2 site in pyroxenes and provide additional information on thermal history. The obtained partitioning coefficient $k_{D*}$ is related to the closure $T_c$ of cation exchange and can provide a
semiquantitative indication of the cooling rate of the host meteorite (Ganguly 1982; Ganguly et al. 1994; Tribaudino et al. 1997; Zema et al. 1997; Domenechetti et al. 2000; Goodrich et al. 2001; Domenechetti et al. 2005). Structural analyses to calibrate cation partitioning mostly have been performed on orthopyroxene, which has a simpler chemistry than pigeonite and shows fewer defects. Cation ordering in pigeonite has been investigated only by Pasqual et al. (2000), who experimentally calibrated the equilibrium \( k_D \) at different temperature in two pigeonites, one from natural volcanic rhyodacite (BTS308) and the other from the ureilite PCA 82506. The Pasqual et al. (2000) calibrations were comparable to those obtained in orthopyroxenes, and for both samples cation ordering fell within expectations for rapidly cooled samples.

Microtextural and cation ordering investigations in pigeonite are of interest in ureilites. Ureilites are a C-rich achondrite group, mostly composed of olivine and pyroxene(s), namely uninverted pigeonite and more rarely augite and/or orthopyroxene. Pigeonite from ureilites differs from that in most terrestrial volcanic samples in having higher mg and higher crystallization temperatures (Mittlefehldt et al. 1998); inversion to orthopyroxene is not observed due to rapid cooling from high temperature.

A number of microtextural investigations have been performed on ureilite pyroxenes (Chikami et al. 1997; Tribaudino et al. 1997; Goodrich et al. 2001; Weber et al. 2003). In two of these studies the microtextural observations were coupled with determination of Fe-Mg cation partitioning in orthopyroxenes (Tribaudino et al. 1997; Goodrich et al. 2001). For ureilite pigeonite, determination of cation ordering coupled with TEM analysis has been done only on PCA 82506 (Pasqual et al. 2000).

It is the purpose of this paper to investigate specifically the microstructures and cation partitioning in pigeonite in ureilites, to characterize the different pigeonite samples, and to assess the potential and limits for gathering information on cooling history from pigeonite. Four samples of different shock level and composition were therefore investigated by means of a combined TEM-XRD single crystal analysis.

**EXPERIMENTAL**

The pigeonite-bearing ureilites ALHA77257, RKPA80239, ALHA81101, and Y-791538 were studied. Samples ALHA77257,124, RKPA80239,14, and ALHA81101,39, weighing 2.5, 2.2, and 2.4 g, respectively, were obtained from the NASA curatorial facility at Johnson Space Center; a sample of Y-791538 weighing 1.6 g was obtained from the National Institute of Polar Research (Japan). A chip of each sample was crushed in order to select single crystals for diffraction and TEM observation; thin sections for SEM (scanning electron microscope) and microprobe analysis were prepared from the remaining part of each sample. As it turned out, microprobe analyses of olivine and pyroxenes were performed on thin sections only for samples ALHA77257 and ALHA81101. The pigeonites in RKPA80239 and Y-791538 were analyzed from a few grains of the crushed portion embedded in epoxy and polished. This was done because the thin section of Y-791538 was lost during thinning and because pigeonite was not present in the RKPA80239 thin section.

Microprobe analyses were determined using a SEM Cambridge S 360 electron microprobe equipped with EDS Link Analytical XQ 2000. Natural oxides and minerals were used as standards. ZAF 4 corrections were applied to the analyses. Analytical results on pyroxenes are reported in Table 1.

A few single crystals of pigeonite from each of the four ureilites were selected on the basis of sharp optical extinction and then tested by X-ray diffractometry; most of the crystals selected turned out not to be suitable for single crystal X-ray diffraction, displaying large and diffuse peak profiles. Full refinements were done for ALHA77257, RKPA80239, and Y-791538 pigeonites, but the RKPA80239 and ALHA77257 data were discarded because the refinement results did not permit reliable cation partitioning. As expected by its highly defective shock overprint, ALHA81101 turned out to be completely unsuitable for data collection. The best crystals for each sample were measured with a Siemens P4 four circle diffractometer.

The data collections were done with the θ-2θ scan type technique using graphite monochromatized MoK\(_\alpha\) radiation (\(λ = 0.71073 \text{ Å}\)), and the reciprocal lattice was explored up to \(θ \leq 30°\). Two sets of equivalent reflections were measured. A correction according to the \(ψ\) scan (North et al. 1968) for absorption did not significantly improve the refinement results.

The structure refinements were completed using SHELXL-97 (Sheldrick 1997), performed in \(P_2_1/c\) space group starting from the atomic coordinates of clinoenstatite (Ohashi and Finger 1976). The refinement reached convergence before the final full-matrix least-squares with chemical constraints was carried out. All Ca and Na were ascribed to the M2 site; Cr was constrained to occupy the M1 site, while Al was partitioned between the T and M1 sites with the condition that \(Cr^{3+} + Al^{IV} = Na + Al^{III}\) to obtain a neutral crystal formula. After partitioning of Al the cation sum in T and M1 + M2 sites were normalized and used as a basis for \(Fe^{2+}\)-Mg partitioning between the M1 and M2 sites. Mn was partitioned as \(Fe^{2+}\) between the M1 and M2 sites. For consistency with previous calibrations, this procedure was preferred over the recommendation of Stimpfl (2005) to ascribe all Mn to the M2 site. The refinement of Mg and \(Fe^{2+}\) site occupancy between the M2 and M1 sites was done with the constraints that: 1) total occupancy of M1 and M2 sites is equal to one, and 2) the \(Fe^{2+}/Mg\) ratio is equal to the analytical value. The error for the chemical constraints was assumed to be 1σ. Standard SHELXL-97 procedures were used for refinement of the Mg and \(Fe^{2+}\) site occupancies; details of the
Table 1. Compositions of pyroxenes in the investigated samples by SEM-EDS analysis on polished thin sections.

<table>
<thead>
<tr>
<th></th>
<th>ALHA77257</th>
<th>Y-791538</th>
<th>RKPA80239</th>
<th>ALHA81101</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>57.3(7)</td>
<td>58.1(7)</td>
<td>55.2(7)</td>
<td>56.1(9)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.70(9)</td>
<td>0.90(10)</td>
<td>0.62(8)</td>
<td>n.d.</td>
</tr>
<tr>
<td>CrO₃</td>
<td>1.13(12)</td>
<td>1.01(15)</td>
<td>1.13(13)</td>
<td>1.3(4)</td>
</tr>
<tr>
<td>FeO</td>
<td>8.4(3)</td>
<td>5.27(16)</td>
<td>9.6(2)</td>
<td>11.1(4)</td>
</tr>
<tr>
<td>MnO</td>
<td>0.51(2)</td>
<td>0.55(8)</td>
<td>0.43(8)</td>
<td>0.5(2)</td>
</tr>
<tr>
<td>MgO</td>
<td>29.7(4)</td>
<td>30.8(4)</td>
<td>28.8(5)</td>
<td>28(2)</td>
</tr>
<tr>
<td>CaO</td>
<td>3.29(12)</td>
<td>4.9(2)</td>
<td>3.23(14)</td>
<td>4(2)</td>
</tr>
<tr>
<td>Total</td>
<td>101(1)</td>
<td>102(1)</td>
<td>99(1)</td>
<td>101(2)</td>
</tr>
</tbody>
</table>

Table 2. Cell parameters, main structural results, and site occupancies of the Y-791538 pigeonite.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V(Å³)</th>
<th>Nₐ₀ (unique)</th>
<th>Rₐ (%)</th>
<th>Rₐ (%)</th>
<th>Goof</th>
<th>M₁ site</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>9.689(3)</td>
<td>8.882(3)</td>
<td>5.212(2)</td>
<td>108.50(3)</td>
<td>1239</td>
<td>7.81</td>
<td>5.71</td>
<td>1.23</td>
<td>0.018</td>
</tr>
</tbody>
</table>

RESULTS

Mineral Chemistry of Pigeonite

Petrographic descriptions previously have been published for the ureilites investigated here (Berkley et al. 1980; Takeda and Yanai 1982; Berkley 1986; Takeda 1987, 1989). In addition, the diamonds in Y-791538 and ALHA77257 have been studied by Nakamuta and Aoki (2000). The petrographic observations made here are consistent with previous results. In particular, ALHA77257, RKPA80239, and Y-791538 display a relatively low-shock texture with crystals sized between 0.1 and 1 mm and...
abundant triple junctions, whereas ALHA81101 has a high-shock overprint with mosaicized olivine and deformed pigeonite. ALHA77257 and RKPA80239 have 5–50 µm wide reduction rims on olivine grains.

SEM-EDS analyses of pyroxenes are reported in Table 1. The analytical dispersion of the analyses is shown in brackets. Cation charge excess is within 0.02 charge unit per formula unit, with the exception of ALHA77257, in which it is as much as 0.06, and in ALHA81101, in which Al possibly could have been overlooked. The analytical results reported in Table 1 are consistent with previous reports on the pigeonites in the meteorites studied. Pigeonite was found in all samples, and in ALHA77257 and Y-791538 orthopyroxene was also found. Orthopyroxene is a main constituent in Y-791538, whereas in ALHA77257 it was found only as one tiny crystal (about 50 µm) within olivine, confirming the previous observation by Takeda (1987). The chemical compositions of the examined pigeonites compared with other ureilites and with terrestrial volcanic pigeonite are reported in Fig. 1. In general, ureilite pigeonites have higher mg than terrestrial volcanic ones; in addition, among ureilites there is significant variation in Ca and mg content. As shown later, this significantly affects the microtextures that are observed, and in part also the reliability of the determined cation partitioning.

The pyroxenes from the low-shock ureilites were found to be compositionally homogeneous, without core-rim zoning (Table 1). In contrast, the pigeonite in ALHA81101 is heterogeneous, with an average composition similar to that of the other samples but large local variations in Wo and mg (4–13 for Wo, and 86–68 for mg). A possible explanation for this heterogeneity is strong elemental mobilization at high temperature due to impact strain. Migration of Ca at grain boundaries of olivine due to shock was found by Saito and Takeda (1990) in the same meteorite. Heterogeneity of pyroxene compositions has been found (e.g., Berkley et al. 1980) in most highly shocked ureilites.

The compositions of the homogeneous pigeonites can be used to estimate crystallization temperatures to within ±20 °C, assuming that they represent olivine-pigeonite-liquidus equilibrium (Singletary and Grove 2003). For the pigeonites in this work, crystallization temperatures were estimated as 1260, 1275, and 1257 °C respectively for ALHA77257, Y-791538, and RKPA80239 using the geothermometric formulation given in Singletary and Grove (2003). These temperatures are consistent with expectations based on the Fo contents of olivine (Singletary and Grove 2003). The results of this work are also in agreement with the estimate of 1240 °C obtained from two-pyroxene thermometry by Takeda (1989) from the pigeonite-orthopyroxene couple in sample Y-791538.

**Microtextures in Pigeonite**

**ALHA77257 and RKPA80239**

TEM observation shows the presence of a lamellar texture in both samples. The lamellae are oriented parallel to (100), are irregularly spaced (on average 8 nm, but with lamellae up to 100 nm wide), and induce a streaking of the diffraction patterns (Figs. 2a–2c). They are interpreted as a pervasive twinning, presumably related to shock, in agreement with previous observations by Mori and Takeda (1988) on the ALHA77257 ureilite. Twinning locally occurs at the unit cell scale; a superstructural periodicity of 1.8 nm and an orthopyroxene-like slab is then observed (Fig. 2b). Repetition of twinning each three or more unit cells is also
observed. TEM-EDS analysis did not show significant chemical differences between twinned and untwinned areas. No exsolution texture, not even in the form of a nonperiodic modulation, was found in these samples; furthermore, peak splitting indicative of exsolution was never found, confirming that the observed lamellae have a crystallographic rather than compositional origin.

Antiphase domains are present in both samples, sized about 150 nm (Fig. 2d), as previously observed in another section of ALHA77257 by Mori and Takeda (1988).

Y-791538

In the Y-791538 pigeonite, pervasive lamellae parallel to (100) are not present; consequently, selected area diffraction patterns do not show significant streaking along a* (Fig. 3a). Diffraction spots show a peak splitting (inset of Fig. 3a), and dark field imaging with h+k even reflections shows a modulation, most prominent parallel to (100) but also parallel to (001) (Fig. 3c). The presence of satellites along a* (Fig. 3a), although they are rather diffuse, indicates that the modulations can be interpreted as incipient spinodal

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Fig. 2. Microtextures in the RKPA80239 and ALHA77257 pigeonites: a) selected area electron diffraction (SAED) pattern in RKPA80239, view along [010]; note streaking along the a* axis, due to stacking disorder; b) lattice image showing 1.8 nm orthopyroxene-like periodicity within 0.9 nm periodicity of pigeonite; c) stacking disorder in ALHA77257, dark field image g = 400; the diffraction pattern is equivalent to that in (a); d) antiphase domains in ALHA77257; dark field g = 012.
decomposition textures (Weinbruch et al. 2003). The modulations along the c* axis are, in contrast, nonperiodic, and in diffraction patterns they are revealed by streaking (Figs. 3a–3c). Elongated antiphase domains 10 nm in size (Fig. 3b), i.e., significantly smaller than in ALHA77257 and RKPA80239, are observed. Smaller-sized domains in connection with compositional modulations have been observed in samples with mottled textures (Tribaudino 2000; Weinbruch et al. 2001) and interpreted as a result of a pinning effect of the Ca-rich region of the modulation to Ca-enriched domain boundaries (Tribaudino et al. 2003). The presence of antiphase domains indicates that the pigeonite crystallized in $C2/c$ symmetry, above the transition to $P2_1/c$. This is in good agreement with thermometric estimates: the critical temperature for the transition can be estimated, for the composition of the Y-791538 pigeonites, to be near 1000 °C (Arlt et al. 2000; Tribaudino et al. 2005).

ALHA81101

In ALHA81101, the major finding was the observation of augite exsolution lamellae in pigeonite (Figs. 4a and 4b). The average size of the pigeonite lamellae is about 120 nm, that of augite 20 nm, the wavelength 140 nm. The exsolution occurs along (001) as confirmed by the analysis of selected area diffraction patterns, showing clear splitting along the c* axis (Fig. 4a), and by TEM-EDS microprobe analysis of the phases. The TEM-EDS analysis of the grain in Fig. 4 reveals a Ca/Si ratio of 0.09 for the host pigeonite, 0.30 for the augite lamella, 0.12 for the bulk crystal, and between 86 and 88 for mg. An alternative determination of lamellar composition was performed measuring in selected area diffraction patterns the differences in β parameter, which is extremely sensitive to the Ca content (Turncock et al. 1973, Gordon et al. 1981) but insensitive to mg. The obtained $\Delta \beta$ between the Ca-rich and Ca-poor phase is 1.26°, which corresponds to a composition of Wo 31 for the clinopyroxene. Application of two-pyroxene thermometry from QUILF (Andersen et al. 1993) to the two-pyroxene pair compositions obtained by TEM-EDS microprobe analysis gives an exsolution $T = 1253(12)$ °C. Owing to the small amount of pigeonite available, a systematic analysis on the sample was not performed, and further investigation may be needed.

DISCUSSION

Crystal Structure and Fe$^{2+}$-Mg Order Disorder

Fe$^{2+}$-Mg site partitioning in Y-791538, as determined by single crystal X-ray diffraction, is reported in Table 2. The $k_D$ partitioning coefficient of the reaction: Fe$_{M2}$ + Mg$_{M1}$ = Mg$_{M2}$...
+ Fe_M1 is also reported, calculated as k_D* = XFe*(M1)[1 – XFe*(M2)] / XFe*(M2)[1 – XFe*(M1)], where XFe*(M1) = (Fe + Mn)_M1 / (Fe + Mn + Mg)_M1 and XFe*(M2) = (Fe + Mn)_M1 / (Fe + Mn + Mg)_M1 (Pasqual et al. 2000). As in any pyroxene, there is a preferential partitioning of Fe^{2+} in the M2 site and of Mg in the M1 site, and cation disorder has to be considered in a relative way. A general rule to interpreting cation partitioning is that higher disorder is related to faster cooling; however, the same k_D in different samples may not a priori indicate the same cooling rate. The effect of different compositions and microstructures also has to be addressed. Following an ideal model, a linear equilibrium relation lnk_D* = a/T + b (Ganguly 1982) was established and has been calibrated for several samples of different mg in orthopyroxene and pigeonite. The differences between orthopyroxene and pigeonite are rather small (Stimpfl et al. 1999; Pasqual et al. 2000), permitting at least a general comparison between them. Namely, the calibration for orthopyroxenes with mg between 89 and 80 (Stimpfl et al. 1999) for orthopyroxene and that of Pasqual et al. (2000) on pigeonite sample from ureilite PCA 82506 (mg = 80) were used in the comparative Fig. 5 (in Zema et al. 1997). The calibration by Pasqual et al. (2000) was used to determine the T_c of the refined sample.

In Fig. 5, comparison with terrestrial volcanic and metamorphic orthopyroxenes and the volcanic pigeonite BTS308 shows that Y-791538 falls within the field of rapidly cooled terrestrial volcanics, close, within error, to the orthopyroxenes from FRO 90054 and Hughes 009 (Tribaudino et al. 1997; Goodrich et al. 2001), and the pigeonite from PCA 82506 (Pasqual et al. 2000).

The presence of a disordered (broadly speaking) configuration is indicative of a rather fast cooling rate. In Hughes 009 orthopyroxene (Goodrich et al. 2001), the cooling rate was estimated at the closure T to be about 7°/h, based on the analysis of single crystals of orthopyroxene.

**Microtextures and Cooling History**

The various pigeonites examined in this study have different compositions and display different microstructures. The ALHA77257 and RKPA80239 pigeonites have a low average Ca content (Wo 6.4) and contain twin lamellae related to stacking disorder and antiphase domains, but no exsolution textures. The lack of exsolution is related to the relatively Ca-poor composition and rapid cooling. These pigeonites crystallized in the single phase field at high temperature, and during cooling intercepted the solvus of Ca-rich and Ca-poor clinopyroxene. Due to the low Ca content the chemical solvus was actually intercepted, but not the spinodal, and exsolution could take place only through nucleation and growth (Fig. 6). Nucleation and growth is more kinetically demanding than spinodal decomposition and could not occur in ALHA77257 and RKPA80239 pigeonites due to relatively fast cooling. The same interpretation can be applied to the lack of exsolution in PCA 82506, which has a similar Ca content, and to the
Fig. 5. $-\ln k_D$ versus $1/T$ in pigeonites (open diamonds) and orthopyroxenes (full squares) in ureilites; $k_D^* = \frac{X_{Fe^*(M1)}[1 - X_{Fe^*(M2)}]}{X_{Fe^*(M2)}[1 - X_{Fe^*(M1)}]}$, where $X_{Fe^*(M1)} = \frac{(Fe + Mn)_{M1}}{(Fe + Mn + Mg)_{M1}}$ and $X_{Fe^*(M2)} = \frac{(Fe + Mn)_{M2}}{(Fe + Mn + Mg)_{M2}}$, was determined from single crystal refinement. The range observed in orthopyroxenes in other achondrites and in terrestrial rocks is reported for comparison; the small diamond refers to the BTS308 pigeonite in rhyodacite (Pasqual et al. 2000). The dashed line indicates the calibration for orthopyroxene by Stimpfl et al. (1999); the range of terrestrial volcanic and metamorphic orthopyroxenes is shown in bold. The two pigeonites lie slightly off the line, as the $1/T$ was obtained by the calibration of Pasqual et al. (2000).

Fig. 6. Phase diagram showing the chemical solvus (solid line) between one-phase pigeonite (Pig) and two-phase pigeonite + augite (Pig + Aug) fields, and the coherent spinodal solvus (dashed line). The chemical solvus was calculated using Andersen et al. (1993) for mg $\sim 92$, as in Y-791538 pigeonite. A decrease in mg to the values by ALHA77257 and RKPA80239 pigeonites decreases the solvus by about 30 °C. Symbols used: diamonds = Y-791538 (Y79, on the right), ALHA77257 and RKPA80239 (Al77/RK80, on the left, overlapping one another) pigeonites at the crystallization T determined by Singletary and Grove (2003); error bar = compositional range of ALHA81101 pigeonite at the T determined by pyroxene exsolution (see text); circle = bulk composition of the grain displaying exsolution in ALHA81101.
pigeonite of Jalanash and HaH 064 ureilites (Wo 7.8 and 4.5, respectively [Weber et al. 2003]). The Y-791538 pigeonite had a higher average Ca content (Wo 9.4); at its formation temperature, it is within the single phase stability field, but during cooling the spinodal solvus is intercepted at a temperature and at a cooling rate sufficient to promote cation diffusion in Ca-richer and Ca-poorer areas.

It must be stressed that in the above interpretation, different cooling rates for Ca-poorer, exsolution-free, and Ca-richer, exsolution-bearing pigeonite are not required. In the analysis of microtextures as related to cooling history, care must be taken to compare compositionally similar samples.

In the case of Y-791538, the lack of experimental calibration of the onset and the evolution of the wavelength of spinodal decomposition in pigeonite limits cooling rate calculations, but end-member conditions can be still defined. At first, assuming that the chemical and spinodal solvi have the same relation as in the Ca-rich region, it can be tentatively assumed that the spinodal solvus is crossed at about 1100 °C for Y-791538 (Fig. 6, based on Jantzen 1984). This can be confirmed by the size and shape of antiphase domains, which as discussed above, require a pinning of local Ca-enrichment; the enrichment should be already present at the transition. As the $P_2_1/c$-$C_2_1/c$ transition occurs at $T = 1000$ °C (Arlt et al. 2000; Tribaudino et al. 2005), the beginning of spinodal decomposition is constrained to a higher temperature.

An indication as to the cooling rate of Y-791538 may come from continuous cooling experiments by Weinbruch et al. (2001). In their experiments, a pigeonite of composition similar to Y-791538 displayed modulated structure only when cooled slower than 50°/h. This condition is consistent with previous determinations on ureilites (Goodrich et al. 2001; Weber et al. 2003), which are on the order of 20°/h at 1100 °C, and with the proposed model of a breakup followed by deep burial in a rubble pile from a single parent body proposed by Goodrich et al. (2004).

The relatively long exsolution wavelength in ALHA81101 indicates slow cooling, on the order of years (Weinbruch and Müller 1995), and is in any case not compatible with fast cooling after breakup. In ureilite pyroxene coarse exsolution lamellae ($\approx$50,000 nm) were found in the LEW 88774 ureilite (Chikami et al. 1997; Goodrich and Keller 2000). These lamellae were interpreted as related to exsolution at high temperature of a single pyroxene of intermediate composition. However, LEW 88774 is one of the most ferroan ureilites (Fo $\sim$75) and therefore is probably formed at much greater depth than the Mg-richer ureilites investigated in this work (Goodrich et al. 2004).

In ALHA81101, the bulk composition is within the compositional field of pigeonite, but shock-induced mobilization produced local Ca-enrichments that pushed the composition towards the two-phase field. In the more Ca-rich areas of ALHA81101, prolonged heating at high temperature after a shock event possibly promoted local exsolution.

Another point is stacking disorder, which was found in the relatively Ca-poor pigeonites, in ALHA77257, and RKPA80239 in this work, and also in Jalanash and HaH 064 (Weber et al. 2003). One interpretation is that stacking disorder results from mild shock (Takeda 1987). However, although both ALHA77257 and Y-791538 were mildly shocked, stacking disorder is very high only in the former. In fact, a chemical constraint is likely: stacking disorder leads to the formation of orthopyroxene lamellae, with a structure locally unfavorable to Ca. In relatively Ca-rich pigeonites the formation of stacking faults during shock is inhibited; however, in relatively Ca-poor pyroxenes subjected to the same degree of shock, stacking disorder will occur.

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