Introduction: Howardites are meteorites made up of polymict breccias which are composed of diverse minerals and lithic clasts. Most of the material is identical or very similar to basaltic eucrites, cumulate eucrites and diogenites. Howardites, eucrites and diogenites (the HED meteorite group) are supposed to have been formed by igneous processes on the same parent body, probably asteroid 4 Vesta.

In a previous study [1] orthopyroxene single-crystals from small fragments of the Kapoeta, Old Homestead 001 and Hughes 004 howardites were studied by X-ray diffraction (XRD) and microprobe analyses (EMPA) and the Fe-Mg equilibrium distribution coefficients $k_D$ of the crystals were used to calculate the closure temperatures using the calibration developed by [2]. The compositions, the presence of exsolved augite lamellae and the $T_c$ values (from 365 to 385°C) obtained for Kapoeta orthopyroxenes suggested that this fragment comes from unheated diogenitic cumulate clasts that experienced very slow cooling. The more Fe-rich composition, the absence of exsolved lamellae and the higher $T_c$ values (from 583 to 605°C) measured in the Old Homestead 001 orthopyroxenes suggested that this fragment comes from eucritic cumulitic clasts quenched at high T. For the Hughes 004 orthopyroxenes, close in composition to Old Homestead 001, the different $T_c$ (339, 358 and 607°C) recorded by the various crystals and the presence of augite lamellae in the crystals with the lowest $T_c$ supported the hypothesis that this howardite sample is an unheated breccia containing a mixture of cumulitic orthopyroxenes with different thermal histories. Therefore the cooling of all Old Homestead and H9 samples was quenched at high temperature by disruptive impacts on still hot plutonic rocks, instead, all the Kapoeta, H1a and H5 samples were ejected by impact on cooled plutonic rocks. There is evidence that the howardites studied were sampled without the thermal memory of the orthopyroxenes being reset, thus supporting the hypothesis that spallation is the most suitable model for the launching of howardites from their parent body, in accordance with Auspaug's model [3].

The aim of the present study was to investigate the trace element distribution of orthopyroxenes from cumulate diogenitic and eucritic clasts [1] in order to focus possible relationships with their petrogenetic and/or thermal history, in particular with the closure temperature of the Fe-Mg exchange reaction.

Experimental Procedure: The same single-crystals used for XRD and EMPA were analyzed by LAM-ICP-MS. The laser probe, installed at the CNR-IGG in Pavia, uses pulsed Nd:YAG laser source “Brilliant” by Quantel whose fundamental emission in the infrared 1064 nm is converted into 266 nm. For this work laser was operated at the repetition rate of 10Hz and the spot was ~40µm with a pulse energy in the range 0.05-0.1 mJ. The particles produced by ablation were then analysed by a field-sector mass spectrometer (“Element”, Finnigan MAT). Ablation signal integration intervals were selected by carefully inspecting time-resolved analysis; data reduction was performed by the software package “LamTrace” developed at MUN. NIST SRM 612 was used as the external standard, while $^{44}$Ca was used as internal standard. Reproducibility and accuracy were assessed on the control sample BCR2-g to be both ~15% relative.

Results and discussion: The chondrite-normalized patterns of minor and trace elements are shown in figure 1 and are in agreement with those measured by [4] for pyroxenes from 4 Vesta. The following elements: Sc, Ti, V, Y, Zr, Nd, Sm, Dy, Ho, Er, Yb and Hf show a positive correlation with $T_c$ while Cr shows an inverse correlation. In particular the relationships between Yb, Zr, Ti and Cr abundances and $T_c$ are reported in figures 2. Kapoeta and Hughes 004 n.1 and n.5 orthopyroxenes, which record the lowest $k_D$ and $T_c$ values, exhibit the lowest REE and HFSE values. Old Homestead 001 and Hughes 004 n.9 orthopyroxenes, which record the largest $k_D$ and $T_c$ values, exhibit the largest REE concentration. It is evident that in the investigated samples the trace and minor element concentrations appear to be more...
closely related to $T_c$ values than to their eucritic or diogenitic origin (and therefore of major element composition), as shown by samples K1 K2, K5, H1 and H5. The depletion of incompatible elements in samples with low $T_c$, namely HREE and HFSE could be explained in terms of compatibility between the octahedral volume and the ion size. This could be also confirmed by the behaviour of the largest LREE ions, like La and Ce that appear not to be correlated with $T_c$. The inverse relationship with $T_c$ shown by Cr could be explained as a substitution induced by charge-balance requirements.

Conclusions: Taking into account the thermal history model data provided in [1] for Kapoeta, Old Homestead and Hughes howardites, the different abundances in REE and HFSE between high and low $T_c$ samples could be interpreted as a slow removal from the lattice structure of incompatible elements as temperature falls. The REE and HFSE depletion with cooling mainly concerns the subsolidus evolution of the investigated samples. Only Cr shows the opposite trend, with higher contents in crystals subjected to a longer cooling history. These results would suggest that the subsolidous cooling history of igneous orthopyroxene, in particular the closure temperature of Fe-Mg exchange reaction, has to be considered when petrogenetic models for estimating parental melt compositions are applied using orthopyroxene trace element partition coefficients.