

MICRO-ZONING IN MINERALS OF A LANDES SILICATE INCLUSION. D. D. Eisenhour¹), P. R. Buseck¹), H. Palme²) and J. Zipfel²); ¹) Departments of Geology and Chemistry, Arizona State University, Tempe, Arizona 85287, USA, ²) Max-Planck-Institut für Chemie, Saarstrasse 23, 6500 Mainz, Germany.

There is an increasing number of meteorites with chondritic bulk composition but completely different textures than the conventional chondrite groups. Winonaites, Acapulcoites and silicate inclusions in IAB-iron meteorites have in common coarse grain size, highly equilibrated mineralogy with frequent 120° triple junctions and they record a significantly lower degree of oxidation than ordinary chondrites. They all have equilibration temperatures, based on Ca-exchange among pyroxenes, of around 900 to 1100°C. However, on cooling disequilibrium features may develop: (a) Olivine in IAB-inclusions has lower Fa-content than equilibrium Fs-content of pyroxenes requires (1) (b) CaO-zoning in olivine was established at temperatures of around 500°C, several hundred degrees below pyroxene equilibration temperatures (2). Obviously, olivine responded faster to changes in fO₂ (Fa in olivine) and temperature (Ca-zoning) than pyroxenes. Differences in diffusion coefficients can readily explain the observed trends. Here we report on much more subtle zoning features in pyroxenes. TEM-observations reveal large compositional gradients in Ca, Na, Cr, Ti and Fe within the first micrometer of cpx and opx crystals.

Experimental: Representative grain boundaries were identified in a Landes thin-section by SEM/EMPA, and then removed from the section and ion-thinned to electron transparency. Analyses were performed on a JEOL 2000FX TEM equipped with a Kevex thin-window, energy-dispersive x-ray spectrometer. A fixed probe diameter of 50 nm and a constant beam current were used for analyses. From time-resolved diffraction and EDS data it was determined that the resulting beam-current density caused no structural damage or volatile element loss from any of the phases analysed. Inter-element K-factors were determined by analyzing cpx, opx, and olivine grain interiors and comparing these values to WDS microprobe data acquired from the same grains prior to removal from the thin section. ZAF corrections to the data were performed using thicknesses determined by oxygen K_α absorption.

Results and discussion: Zonation profiles in cpx and opx are shown in the Figure. Results are given as number of atoms per 4 cations. Element concentrations 2 μm from grain boundaries are typical of the concentrations for average Landes inclusions and agree with literature data. Extensive zoning begins at a distance of 0.5 to 1 μm from grain boundaries. Some "large scale zoning" of Ca in opx is common in Landes inclusions (3) and can be easily determined with the electron microprobe. According to the calibrations of (4), Ca in opx cores records temperatures of about 980°C, while the lower Ca at opx rims reflects temperatures of about 840°C. A temperature decrease produces a CaO decrease in opx and an increase in coexisting cpx. Surprisingly, Ca decreases in both cpx and opx within the first μm of their boundaries. The decrease of Ca in cpx appears to be compensated by an increase in Na. The combination of both would, according to the formalism of (4), result from an overall small temperature decrease. The parallel increase of Cr suggests that one Cr and one Na ion may substitute for Ca + Mg. The driving force for this replacement could be the formation of Ca-phosphate which is commonly found in these inclusions. Cpx may then act as a source for Ca.

Formation of Ca-phosphate would also provide an explanation for the FeO-zoning since it involves the oxidation of metallic P to P-oxide and a simultaneous reduction of FeO to Fe. Since diffusion in olivine is much faster than in pyroxenes, olivine crystals would be affected much more than pyroxene-crystals. According to calculations by (5), the transition of P dissolved in NiFe to phosphate would occur in Landes silicate inclusions at temperatures below 830°C.

The zoning of Cr, Ti, (see Figure) and also Zr (not shown in the Figure) in cpx is difficult to understand. As temperature decreases both Cr and Ti will, under equilibrium conditions, begin to move from opx into cpx just as Ca would have done in the absence of phosphate formation. In addition, both Cr and Ti may be required for charge balance to compensate for the loss of Ca.

The enrichment of Na in the outer layers of cpx requires a Na source. The only reasonable source is plagioclase. A grain of Al-silicate was found associated with plagioclase, providing evidence for dissolution of plagioclase and diffusion of Na into cpx.

In summary, the data presented here reflect the complicated subsolidus history of a chondritic mineral assemblage that was in thermodynamic equilibrium at about 900°C and cooled slowly from this temperature whereby oxidation reactions and different closure temperatures for various minerals and elements played an important role. The oxidation of P dissolved in metal and formation of phosphate, which is thermodynamically stable at low temperatures, is suggested to be responsible for most of the observed zoning.

MICRO-ZONING IN MINERALS: Eisenhour D. D. et al.

Lit.: (1) v. Seckendorff V. et al. (1992), *Meteoritics* **27**, 288-289; (2) Köhler T. et al. (1991), *N. Jb. Miner. Mh.* **9**, 423-431; (3) Luzius-Lange D. (1986), Ph. D. Thesis, Universität Mainz; (4) Brey G.P. and Köhler T. P. (1990), *J. Petrol.* **31**, 1313-1352; (5) Olsen E. and Fuchs L.H. (1967) *Icarus* **6**, 242-253.

