EVOLUTION OF PYROXENE COMPOSITION DURING CAI FORMATION IN CV3-CHONDRITE NORTHWEST AFRICA 12590.
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Introduction: Refractory Ca-Al inclusions (CAI) are the oldest and most primitive objects formed in the infant solar system [1] with, however, complex history and modifications by subsequent events. CV3 chondrites often contain CAI of various types and new findings are extremely important. The new CV3 chondrite Northwest Africa (NWA) 12590 [2] is enriched in exceptionally unaltered CAIs (Fig. 1). Here we report results on the mineralogical study of clinopyroxenes (Cpx) in the B1- and B2-type CAIs. Pyroxene composition corresponds to Ti-Cpx - grossmanite series and contains a high TiO_x. We have identified several generations of Cpx with different textural features and Ti^{3+}/Ti^{4+} ratios indicating variations of the redox state during CAI formation.

Methods: The mineral composition in B1 type inclusions from polished plates of NWA 12590 was obtained by Oxford X-Max^N EDS spectrometer installed on the JEOL JSM-6480 SEM.

Fig. 1. Examples of sample sections prepared from NWA 12590 CV3 chondrite with fresh CAI inclusions.

Results: We distinguished four groups of CPx in the B1-type CAI from NWA 12590: (I) subhedral crystals up to 500 μm in a central part of inclusions coexisting with melilite and spinel grains (Fig. 2a); (II) Small interstitial Ti-clinopyroxene - grossmanite grains sized up to 5-10 μm (Fig. 2a); (III) small grains up to 15 μm in the boundary zones of inclusions, which have the highest TiO_2 contents (Fig. 2b); (IV) diopside - kushiroite - grossmanite aggregates forming Wark-Lovering (WL) rim (Fig. 2b). Cpx similar to that in WL-rims was occasionally found in the central parts of CAI (Gr. IVa), however, it always has evidence of recrystallization (Fig. 3). The compositions of clinopyroxene types are shown in Table 1 and Fig.4.

The other minerals in CAI are represented by spinel, low-Ti Cpx (up to 2.9 wt.% TiO_2), melilite, anorthite, and perovskite. Calcite may penetrate into CAI along fractures (e.g., Fig.3). WL rims are decorated by spinel from the CAI side and by melilite or low-Ti diopside from the matrix side (Fig 2b).

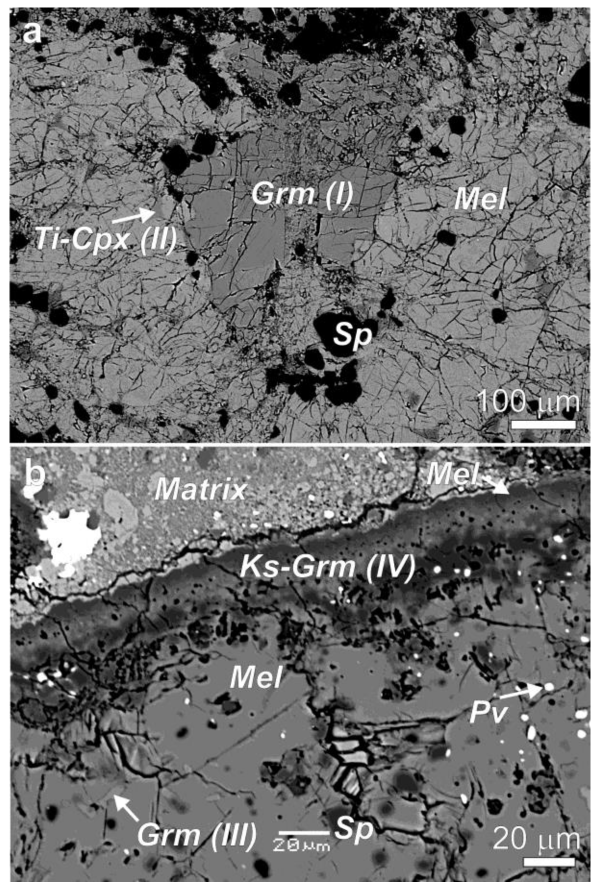

Fig. 2. BSE images of B1-type CAI from NWA 12590 chondrite. (a) central part with large crystal of grossmanite (Grm, Gr. I) coexists with melilite (Mel) and Ti-bearing fassaite-grossmanite (Ti-Cpx, Gr. II); (b) boundary zone with WL-rim containing kushiroite-grossmanite (Ks-Grm, Gr. IV) and Gr. III grossmanite. Dp – diopside, Sp – spinel, Prv – perovskite.

Discussion: Gr. I grossmanite with high Ti^{3+}/ Ti^{4+} ratios (~1.9) represents the initial (or earliest) Cpx generation of CAI formed in the reduced environments. The other groups correspond to different types of modifications indicating progressive depletion in Ti (Gr. II) or oxidation of Ti^{3+} in the reactionary melts [3]. It is also clear, that crystals grew in the melt which was isolated from nebular gas.

Gr. II Ti-Cpx represents the late stages of CAI evolution with partial reactionary re-melting. The composition of Gr. II Cpx is transitional between Gr. I grossmanite and bulk low-Ti Cpx. However, this transition is sharp with a compositional gap between TiO_x = 2.9 and 6.0 wt%.

Rare small grains of grossmanite (Gr. III) near the boundary zones of CAI may reflect crystallization from the melt formed by significant dissolution of perovskite [4, 5], thus approaching highest TiO_x contents up to 20.7 wt.%.

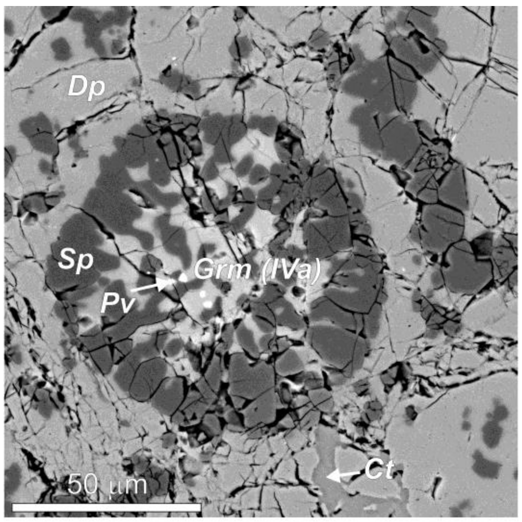

Fig. 3. BSE images of rounded segregation (palisade body) in the central part of B1-type CAI with Gr. IVa grossmanite (Grm), Ct - calcite.

Table 1. Average clinopyroxene compositions (wt.%)

Group	I	II	III	IV	IVa
N	29	12	3	6	6
SiO_2	34.49	38.19	28.74	30.70	33.16
TiO_2	4.92	3.46	8.10	8.12	9.13
Ti_2O_3	8.74	5.56	10.11	3.95	5.64
Al_2O_3	18.71	18.06	22.93	23.93	18.00
FeO	0.01	0.16	0.48	0.57	n.a.
MgO	7.86	9.29	5.19	7.06	8.87
CaO	24.70	25.00	24.15	23.99	25.02
V_2O_3	0.43	0.37	0.79	0.47	0.38
Total	99.86	100.1	100.5	98.79	100.2
TiO_x*	13.66	9.02	18.21	12.07	14.77

TiO_x* = TiO_2+Ti_2O_3. N – number of analyses.

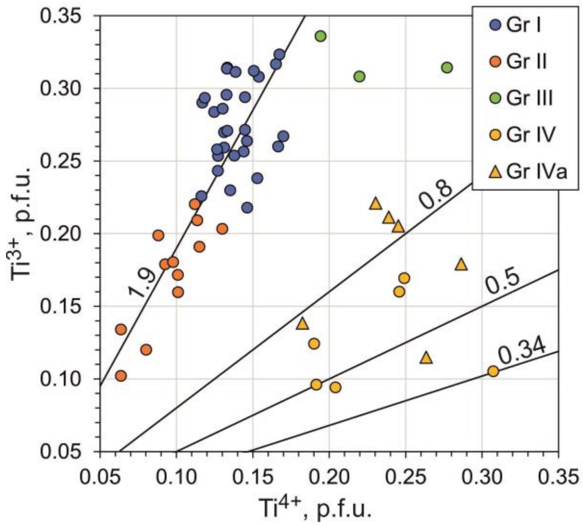

Fig. 4. Ti^{3+} vs Ti^{4+} plot for clinopyroxene in B1-type CAL from NWA 12590 CV3 chondrite. Lines show Ti^{3+}/Ti^{4+} ratios.

Kushiroite-grossmanite Cpx (Gr. IV) with low Ti^{3+}/Ti^{4+} ratios (0.34-0.68) in WL-rim is formed by secondary processes, possibly during erosion of primary CAI or due to exchange reactions between CAI and surrounding materials, but before adjustment to chondrite matrix.

Diopside-grossmanite Cpx (Gr. IVa) with variable compositions close to that in WL rims indicates penetration of matrix material into CAI (sometimes marked as calcite veinlets, Fig. 3) and partial reactionary recrystallization of CAI material. Although Cpx in Gr. IVa is very similar with that in WL (Gr. IV) most likely this process was after the formation of WL rims.

References: [1] MacPherson G. J. (2014) In: *Treatise on Geochemistry (2nd ed.), v.1, Meteorites, Comets and Planets*, Elsevier, p. 139-179. [2] Glazovskaya L. I. et al. (2020) *LPSC 51*, #1090. [3] Simon S. B. et al. (1991) *GCA 55*, 2635-2655. [4] Simon S. B. et al. (2007) *GCA 71*, 3098-3118. [5] Paque J. M. et al. (2009) *MAPS 44*, 665-687.