ORIENTED CHROMITE-DIOPSIDE SYMPLECTIC INCLUSIONS IN LUNAR OLIVINE FROM THE "LUNA-24 SOIL": HYDROGENATION-DEHYDROGENATION AS A MECHANISM OF SYMPLECTIC FORMATION?

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Introduction: Oriented pyroxene-spinel symplectic inclusions were observed in olivines from terrestrial [1-4] and lunar [5-8] rocks as well as from martian meteorites [9-11]. The origin of the spinel-pyroxene symplectites is still debated and several formation mechanisms were suggested: (a) oxidation and exsolution [2, 9]; (b) oxidation and cellular decomposition [1, 3, 4]; (c) breakdown of a precursor phase [5, 7- 9]; (d) crystallization of trapped late-stage melt [5, 6]; (e) diffusion of trace elements out of olivine [6] or reaction between olivine and plagioclase [6]. Here we report and discuss the results of FE-EMPA and FIB/TEM examination of the oriented symplectic inclusions in the olivine grain from the lunar soil delivered by the "Luna-24" soviet mission.

Results: The lunar olivine Fa76.5 is depleted in Ca (up to 0.28 wt. % of CaO) and Cr (up to 0.155 wt. % of Cr_2O_3) and contains a system of Ca,Cr-rich symplectic lamellae of about 1 µm in thickness oriented parallel to each other (Fig. 1).
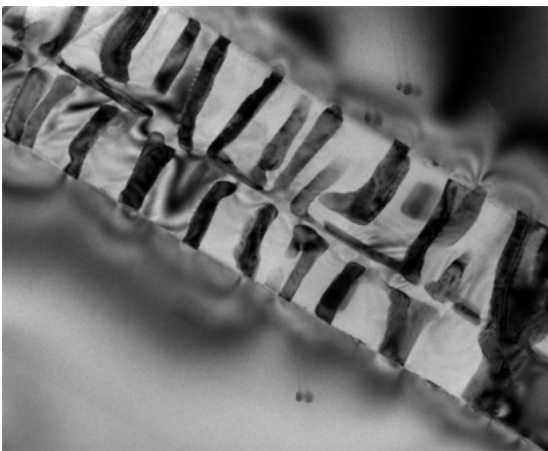

Fig. 1. TEM image of symplectic lamellae in lunar olivine. Black – chromite, white – diopside. Olivine/lamellae interface is parallel to (100) of olivine.

The lamellae occur mostly in the interior of the grain far from the grain surface and are not associated with cracks. They are seldom and irregulary distributed in the grain. The lamellae are composed of a worm-like two-phase intergrowth with an average spacing in the range of 180 – 220 nm.Combining FE-EMPA and TEM data we conclude that the symplectitic inclusions are composed of rod-like chromite and diopside intergrowth; the modal and chemical bulk compositions of the symplectic lamellae are 2Di + Chr and $Ca_2Mg_2Cr_2Fe(SiO_4)_4$ respectively. Chromite, diopside and the olivine host are oriented to each other with $(100)_{Ol}$ // $(111)_{Chr}$ // $(100)_{Di}$; $(001)_{Ol}$ // $(011)_{Chr}$ // $(010)_{Di}$; $[010]_{Ol}$ // $[211]_{Chr}$ // $[001]_{Di}$; $[001]_{Ol}$ // $[011]_{Chr}$ // $[010]_{Di}$. The lamella/olivine interface is flat and parallel to (100) olivine. The chromite-diopside intergrowth attained a "cellular" microstructure.

The FE-EMPA mixed chemical compositions data of lamellae+olivine host reveal a good positive correlation between Ca and Cr in lamellae with a Ca:Cr ratio as 1:1 and verify a Ca + Cr = -2Mg and a 2Cr = - Fe negative correlations reported earlier (Khisina et al 2011). Concentration profiles for Ca measured along the olivine - symplectic lamelle – olivine lines (Fig.2) show Ca depletion zones from both sides of the lamellae close to the lamellae/olivine interface. Cr concentration profile doesn't exhibit a depletion zone in the vicinity of the lamellae.
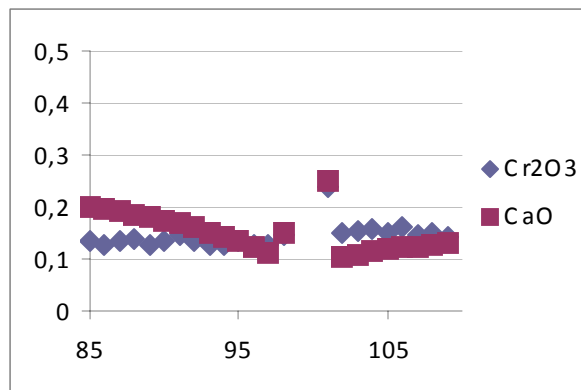

Fig. 2. Concentration profiles for Ca and Cr along olivine host – symplectic lamellae - olivine host 1 mkm-step line.

Discussion: Concentration profile of Ca is typical for a downhill diffusion during heterogeneous nucleation and growth process and confirm that Ca enrichment in the lamellae is due to diffusion of Ca from the adjacent olivine matrix. An absence of depletion zone at the concentration profile of Cr might indicate that chromium which presents in the lamellae now and chromium which diffused before from the olivine host, are to be of different valence state. Chromium in the

lamellae is Cr^{3+}. If the chromium moving from the olivine matrix to the lamellae were Cr^{3+} too, then we should observe the Cr concentration profile similar to that of Ca. As far as depletion zones for Cr are not observed we conclude that chromium diffused as Cr^{2+} from the olivine to the lamellae and changed a charge Cr^{2+}- Cr^{3+} at the lamellae/olivine interface at entry the lamellae. Driving force for Cr diffusion should be an increased electrochemical potential of oxygen at the lamellae/olivine interface, and the latter should be served as a reaction front of oxidation. Different shape of concentration profiles for Ca and Cr indicate that driving forces for Ca and Cr diffusion from the olivine matrix to the lamellae were different and thus Ca and Cr were involved in two different processes and diffused from the olivine matrix to the lamellae not simultaneously. This means that the symplectic inclusion have been formed by a two-step mechanism, resulted in (1) a formation of homogeneous Ca-rich lamellae at the first stage, followed by (2) a cellular decomposition of the lamellae into two-phase intergrowth at the second one. Ca diffusion is associated with the step (1) of lamellae formation, whereas both Cr diffusion and oxidation process are associated with a step (2) of cellular decomposition. We suggest that lamellar symplectic inclusions are associated with deformation features in olivine, which could have provided the nucleation sites for subsequent reactions. Symplectic lamellae inherited a shape of (100) slip band with (100) slip band/olivine interface served as a reaction front of the reactions (1) and (2).

Dehydration as a mechanism of oxidation? There are two different mechanisms of oxidation of nominally anhydrous silicates including olivine: an oxidation of a so-called "dry" olivine due to increased oxygen fugacity $3Me^{2+} +1/2O_2 \rightarrow 2Me^{3+} + v(Me^{2+})_{M1} + MeO$, and a dehydrogenation-oxidation of "wet" (OH^-bearing) olivine due to a shift of H_2O/O_2 buffer equilibrium $2Me^{2+} + \{2OH^- + vM1\} \rightarrow 2Me^{3+} + 2O^{2-} + vM1 + H_2 \uparrow$, where Me = Fe or Cr. Our observations are not consistent with a "dry" olivine oxidation because (i) no oxide precipitation at the cracks was observed with TEM in the vicinity of lamellae; (ii) contrary to the mechanism of "dry" oxidation, Cr moved *across* the olivine/lamellae interface served as a reaction front, with forming the oxidation products *after* crossing the interface; (iii) both morphology and chemical composition of phase constituents in symplectites are not consistent with known products of "dry" olivine oxidation. The latter never contain Ca-clinopyroxene and exhibit not a cellular but granular microstructure or form an (001) olivine-laihunite layered intergrowth; (iv) the products of "dry" oxidation are associated with the host olivine grain boundaries or microcracks, and they were never observed in the olivine grain interior far from the grain boundaries as do the symplectic lamellae. Thus a dehydrogenation is suggested as a mechanism of oxidation and symplectite formation.

Conclusion. Symplectitic inclusions have been formed by a two-step solid-state reaction in olivine without adding of Ca and Cr from the outside of olivine. This proceed by a growing of homogeneous Ca-rich lamellae at the step (1) and a subsequent formation of cellular microstructure in the lamellae due to Cr diffusion from the host olivine to the lamellae and Cr^{2+} $\rightarrow Cr^{3+}$ oxidation under Cr entry the lamellae at the step (2). Diffusion and condensation of OH^- -bearing point defects together with Ca^{2+} inside the deformation-induced precursor at the step (1) and oxidation due to dehydrogenation as a mechanism operated at the step (2) are suggested to be responsible for the symplectic inclusions origin [12]. The oriented symplectites in olivine from lunar, martian and terrestrial rocks, are similar by their shape, strong crystallographic orientation in the host olivine, and worm-like inner texture formed by spinel-clinopyroxene intergrowth. Thus a mechanism of oxidation resulted in formation of symplectite inclusions in all the environments mentioned above should be the same. The main difference between lunar, martian and terrestrial symplectite inclusions is a different composition of a spinel phase represented by chromite in lunar symplectites but magnetite/Al-spinel/chromite and magnetite/Al-spinel in martian and terrestrial symplectites, respectively. This difference is clearly due to different fO_2 conditions on these three planets: IW > log fO_2 > IW-2 on the Moon, IW < log fO_2 < IW+2 on the Mars and IW < log fO_2 < IW + 4 on the Earth [13].

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