Lunar Sample 15421,67: Enigmatic Magnesio-hornblende Monocrystal Hosting Almandine, Omphacite, Quartz, Epidote, Osumilite-Mg, and Al_2SiO_5

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Introduction: A handpicked grain from Apollo 15 (Spur Crater, Station 7) sample 15421,67, was analyzed by EPMA (JEOL JXA 8530F) and Raman (Renishaw inVia Raman microscope, 785 nm) techniques. Both techniques confirmed that the fragment is a crystal of magnesio-hornblende (Mg-hb) with mineral inclusions.

Fragment Description: Sample identified as #S7B9 is a transparent greenish, ~ 550/400 µm-sized fragment (Fig. 1) consisting of one large Mg-hb crystal hosting several rounded and subhedral inclusions (5-90 µm) identified as almandine-rich garnet, zoisite-epidote, quartz, rutile. Quartz hosts small inclusions of omphacite (omph) associated with osumilite-Mg and rutile. Garnet includes micron-size Al_2SiO_5 crystals (kyanite or sillimanite?).

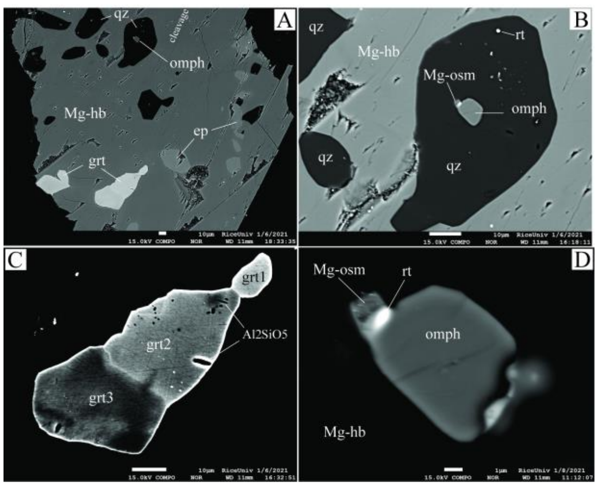

Fig. 1: A: Monocrystal of Magnesio-hornblende (Mg-hb) hosting inclusions: almandine-rich garnet (grt), zoisite-epidote (ep), quartz (qz), omphacite (omph); B: detail of omphacite associated with osumilite-Mg (Mg-osm) and rutile (rt) as inclusions in quartz; C) Three compositionally different annealed crystals of almandine-rich garnet; D: Detail of omphacite (omph), osumilite-Mg (Mg-osm) and rutile (rt) included in quartz (qz). BSE images.

Amphibole: In lunar samples this is rare and/or controversial [1]. The OH-bearing amphibole described herein represents a clear occurrence of amphibole, displaying prismatic cleavage and inclusions (Fig. 1A). The amphibole pattern and OH component were confirmed by Raman analysis (Fig. 2). The average of 15 EPMA analyses, calculated following the IMA 2012 rules [2], shows that the composition of the amphibole is homogeneous, with the formula $(Na_{0.367}K_{0.086})_{\Sigma 0.453}(Ca_{1.456}Na_{0.463}Fe_{0.076}Mn_{0.005})_{\Sigma 2}(Mg_{2.824}Fe^{2+}_{1.073}Al_{0.919}Fe^{3+}_{0.142}Ti_{0.04}Cr_{0.002})_{\Sigma 5}[Si_{6.868}Al_{1.132}]_{\Sigma 8}O_{22}(OH)_2$ and represents a sub-calcic (Na-rich) magnesio-hornblende. Fluorine and chlorine are present in concentrations ~ 0.05 wt%.

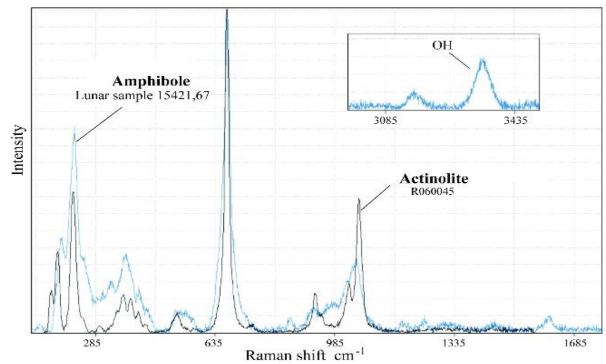

Fig. 2: Raman spectra of amphibole (lunar sample 15421,67, this study) matches 90% the amphibole "actinolite R060045" (Rruff database [3]).

Garnet: Appearing as annealed, anhedral crystals showing a slightly different composition between individual grains. The Raman spectra directly match terrestrial almandine. The composition varies from the brightest ($Alm_{59}Gros_{23}Pyr_{16}Spes_2$) to the darkest ($Alm_{52}Gros_{23}Py_{23}Spes_1$) in Fig. 1C. It contains micron-sized inclusions of rutile and acicular aluminum silicate with the formula $(Al_{1.78}Fe^{3+}_{0.22})_{\Sigma 2}Si_{1.01}O_5$.

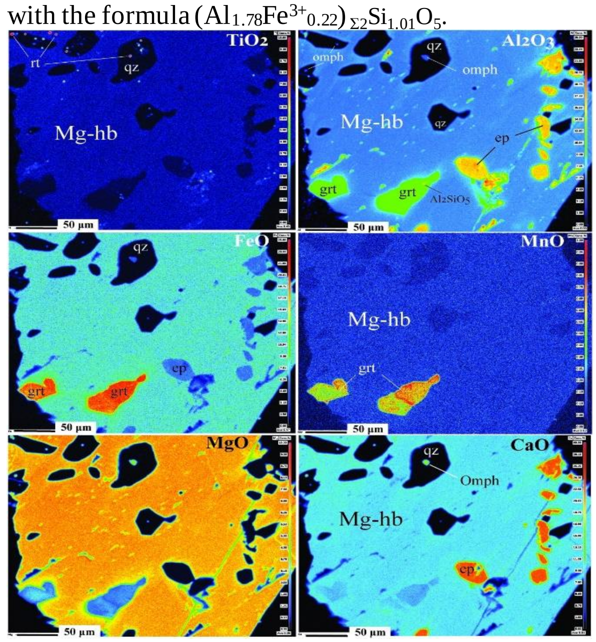

Fig. 3: WDS element maps of Mg-hb and its inclusions.

Omphacite: Identified as ~10-micron grains located in the central part of the observed quartz. The composition $(Ca_{0.588}Na_{0.374}Mg_{0.037}Mn_{0.001})_{\Sigma 1.000}(Mg_{0.458}Al_{0.361}Fe^{2+}_{0.161}Fe^{3+}_{0.017}Ti_{0.02}Cr_{0.001})_{\Sigma 1.000}[Si_{1.991}Al_{0.009}]_{\Sigma 2.000}O_6$ corresponds to $Di_{61.1}Jd_{37.5}Aeg_{1.4}$. On the margin of one omphacite inclusion occurs a 5-micron crystal of osumilite-Mg associated with 1-2 micron size rutile. The osumilite-Mg has an uncommon composition, having significant Fe^{3+} (calculated by charge balance and stoichiometry) replacing Al, and excess Mg: $(K_{1.393}Na_{0.004})_{\Sigma 1.397}(Mg_{2.453}Fe^{3+}_{1.634}Ti_{0.724}Al_{0.089})_{\Sigma 4.900}[Si_{9.635}Al_{2.365}]_{\Sigma 12.000}O_{30}$.

Silica: Occuring as rounded inclusions and is probably quartz, as EPMA indicates ~100% SiO_2 (with minor FeO ~ 0.26 wt%) and several Raman spectra of this phase (Fig. 4) show the main peak at ~ 464 cm^{-1} which fits quartz [3]. However, the peak at 671 cm^{-1} is unique when compared to any known high-P or high-T SiO_2 polymorph (for clarity, Fig. 4 shows a comparison with quartz, coesite, and stishovite, only (Ruff database [3]). It is uncertain if the enigmatic peak represents a possible transition from a relict high-PT phase or it is given by the host amphibole, which also has the main peak at ~ 670 cm^{-1} (see Fig. 2).

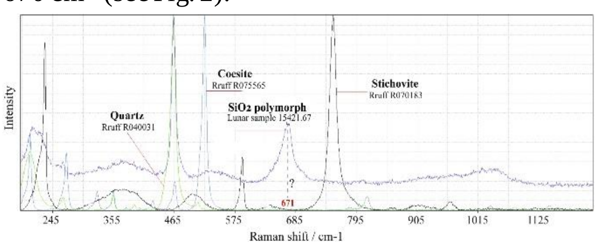

***Fig. 4**. Spectra of SiO_2 phase (Lunar sample 15421.67) compared to quartz, coesite, and stishovite (Ruff database[3])*

Zoisite-epidote: Inclusions in magnesio-hornblende are subhedral and developed as schlieren (Fig. 1). The composition is identified as $(Ca_{1.94}Mg_{0.02})_{\Sigma 1.96}(Al_{2.60}Fe^{3+}_{0.38}Fe^{2+}_{0.04}Ti_{0.01})_{\Sigma 3.03}(Si_{1.00}O_4)[(Si_{1.95}Al_{0.05})_{\Sigma 2}O_7]O(OH)_{\Sigma 2}$ and fits zoisite ($Al:Fe^{3+}>2/1$). The OH content was confirmed by Raman. Yet, when comparing the Raman spectrum of this phase with spectra of zoisite, epidote, and actinolite we find dissimilarities indicating this inclusion do not directly match zoisite but share certain peaks with actinolite and others with epidote.

Discussion: The fragment of a large crystal of magnesio-hornblende hosting almandine, quartz, zoisite-epidote, osumilite-Mg, rutile, and Al_2SiO_5 inclusions represents a unique finding among the lunar soil samples. The mineral inclusions and microtextural aspect suggest the existence of two different assemblages corresponding to two different PT conditions: (1) omph – grt – qz – Mg-osm – Al_2SiO_5 - rt representing high-PT conditions and (2) Mg-hb – alm – zo-ep - qz, probably representing slow subsolidus re-equilibration at lower PT conditions. By intersecting the garnet-omphacite thermometer [4] with the jadeite-in-omphacite barometer we obtain for assemblage (1) a minimum pressure of roughly 1.5 GPa at T ~ 730 Cº. The garnet-amphibole thermometer [5] and Al-in-hornblende barometer [6] suggest that assemblage (2) was equilibrated at T~ 620 Cº and P ~ 0.6 GPa. The precise origin of the components within the 15421,67 split is enigmatic and may be speculative. This is the first finding of omphacite in a lunar soil sample. Also, the low-Ti, OH-bearing amphibole is so far not clearly documented on the Moon. Rare amphiboles (winchite and barroisite) were identified filling voids and veins as metamorphic alteration of chondritic meteorites [7]. However, the bulk composition of the sample 15421,67 (estimated from modal mineralogy) approximates a mela-norite, which is improbable to represent a chondritic provenance but fits a common petrographic component on the Moon. If this sample is not a meteorite, but represents a lunar protolith, then it is a metamorphic lunar rock, which possibly experienced an impact-related high-pressure stage, followed by a slow re-equilibration and re-crystalization to lower PT conditions. The high-water content in phases as amphibole and zoisite-epidote points to an impact with a volatile-rich asteroid, where melting of the norite protolith in the presence of H_2O should have been also involved. It is experimentally known [8], that high-H_2O andesitic liquids stabilize garnet and amphibole as liquidus phases before plagioclase and clinopyroxene (with garnet stable at P > 0.5 GPa). Theoretically, a liquid with the composition (7Enstatite + 4Ferrosilite + 4Anorthite + $2H_2O$) can iso-chemically produce Mg-Hornblende + Pyrope + Almandine + Zo(Ep) + $2SiO_2$, explaining the observed mineral assemblage. Therefore, sample 15421,67 could potentially represent a rare product resulted from deep crystallization of a hydrous, low-Ti, noritic magma derived from an impact with an H_2O-rich asteroid. Slow cooling and re-equilibration (metamorphism) of garnet-amphibole-zoisite-quartz assemblage drove Mg-Fe exchange reactions producing the observed composition of almandine, magnesio-hornblende, zoisite-epidote through reactions as Fe-pargasite + pyrope = Mg-pargasite + almandine [5] and enrichment of zoisite-epidote in Fe^{3+}. The high Fe^{3+} content estimated in osumilite-Mg (assemblage 1) and zoisite-epidote (assemblage 2) suggests high oxygen fugacities during the entire sub-solidus evolution.

References: [1] Treiman, A.H. (2008). Am. Mineral., 93, pages 488–491; [2] – Locock, A.J. (2014). Computers & Geosciences, 6, 1-11; [3] Lafuente et al. (2015) in Highlights in Mineralogical Crystallography, eds. Berlin, Germany, W. De Gruyter, pp 1-30; [4] Ellis, D.J. & Green, D.H. (1979). Contrib Mineral Petrol, 71, 13-22; [5] Graham, C.M. and Powell, R. (1984), J. of Metamorphic Geology, 2: 13-31; [6] Hammarstrom, J. M., and E.-A. Zen (1986), Am. Mineral., 71, 1297,1986; [7] Dobrică, E. and Brearley, A.J. (2014), Meteorit Planet Sci, 49: 1323-1349; [8] Alonso-Perez R, Müntener O, Ulmer P (2009), Contrib Mineral Petrol 157(4),541–558.