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Revision 2

Hutcheonite, $Ca_3Ti_2(SiAl_2)O_{12}$, a new garnet mineral from the Allende meteorite: An alteration phase in a Ca-Al-rich inclusion

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ABSTRACT

Hutcheonite (IMA 2013-029), $Ca_3Ti_2(SiAl_2)O_{12}$, is a new garnet mineral that occurs with monticellite, grossular and wadalite in secondary alteration areas along some cracks between primary melilite, spinel and Ti,Al-diopside in a Type B1 FUN (Fractionation and Unidentified Nuclear effects) Ca-Al-rich inclusion (CAI) *Egg-3* from the Allende CV (Vigarano type) carbonaceous chondrite. The mean chemical composition of type hutcheonite by electron probe microanalysis is (wt%) CaO 34.6, TiO_2 25.3, SiO_2 20.9, Al_2O_3 15.7, MgO 2.1, FeO 0.7, V_2O_3 0.5, total 99.8, giving rise to an empirical formula of $Ca_{2.99}(Ti^{4+}{}_{1.53}Mg_{0.25}Al_{0.17}Fe^{2+}{}_{0.05}V^{3+}{}_{0.03})(Si_{1.68}Al_{1.32})O_{12}$. The end-member formula is $Ca_3Ti_2(SiAl_2)O_{12}$. Hutcheonite has the *Ia-3d* garnet structure with a = 11.843 Å, V = 1661.06 Å^3, and Z = 8, as revealed by electron back-scatter diffraction. The calculated density using the measured composition is 3.86 g/cm^3. Hutcheonite is a new secondary phase in Allende, apparently formed by iron-alkali-halogen metasomatic alteration of the primary CAI phases like melilite, perovskite, and Ti,Al-diopside on the CV chondrite parent asteroid. Formation of the secondary Ti-rich minerals like hutcheonite during the metasomatic alteration of the Allende CAIs suggests some mobility of Ti during the alteration. The mineral name is in honor of Ian D. Hutcheon, cosmochemist at Lawrence Livermore National Laboratory, California, USA.

Keywords: hutcheonite, $Ca_3Ti_2(SiAl_2)O_{12}$, new mineral, schorlomite group, garnet supergroup, Allende meteorite, carbonaceous chondrite, Ca-Al-rich inclusion

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INTRODUCTION

During a nanomineralogy investigation of the Allende meteorite, a new Ti-rich silicate, $Ca_3Ti_2(SiAl_2)O_{12}$ with the *Ia-3d* garnet structure, named “hutcheonite”, was identified in a Ca-Al-rich inclusion (CAI) *Egg-3* (Fig. 1). The Allende meteorite, which fell at Pueblito de Allende, Chihuahua, Mexico on February 8, 1969, is a CV3 (Vigarano type) carbonaceous chondrite. *Egg-3* is a coarse-grained igneous Type B1 FUN (Fractionation and Unidentified Nuclear effects) CAI from Allende (Wasserburg et al. 2012).

Electron probe microanalysis (EPMA), high-resolution scanning electron microscope (SEM) and electron back-scatter diffraction (EBSD) have been used to characterize its composition and structure. Synthetic $Ca_3Ti_2(SiAl_2)O_{12}$ has not been reported to date. However, Grew et al. (2013) suggested that the Ti-Zr-Al-rich garnet (schorlomite) reported by Koritnig et al. (1978) from the Harz Mountains, Germany, could be a natural Al-dominant analogue of schorlomite. We describe here the first occurrence of $Ca_3Ti_2(SiAl_2)O_{12}$ in a meteorite, as a new mineral, being an alteration phase in a CAI from a carbonaceous chondrite, and discuss its origin and significance for secondary alteration processes that affected CV chondrites (e.g., Brearley and Krot 2012 and references therein).

MINERAL NAME AND TYPE MATERIAL

The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2013-029) (Ma and Krot 2013). The mineral name is in honor of Ian D. Hutcheon (born in 1947), cosmochemist and physicist at Lawrence Livermore National Laboratory, Livermore, California, USA, for his many contributions to cosmochemistry and meteorite research. The type specimen is in section MQM803 in G. J. Wasserburg’s Meteorite Collection of Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA.

APPEARANCE, PHYSICAL, AND OPTICAL PROPERTIES

Hutcheonite occurs as small irregular single crystals, 500 nm – 4 μm in size (Figs. 2–3), which are the holotype material. Color, lustre, streak, hardness, tenacity, cleavage, fracture, density, and optical properties could not be determined because of the small grain size. Hutcheonite is non-cathodoluminescent under the electron beam in an SEM. The calculated density is 3.86 g/cm^3 using the empirical formula.

OCCURRENCE AND ASSOCIATED MINERALS

Hutcheonite occurs alone or in contact with monticellite, grossular and wadalite in alteration areas along some cracks between primary melilite, spinel and Ti,Al-diopside in the core area of the CAI (Figs. 1–3). Melilite with spinel, Ti,Al-diopside and anorthite occupies the mantle-core area with a Wark-Lovering rim consisting of Ti,Al-diopside and forsterite. Other secondary phases found in the CAI include nepheline, sodalite, celsian and Na-rich melilite. Trace of Ni-Fe-rich metal is present in *Egg-3*. The matrix around the CAI consists of ferroan olivine, nepheline, diopside-hedenbergite pyroxenes, and minor troilite and pentlandite.

CHEMICAL COMPOSITION

Backscatter electron (BSE) images were obtained using a ZEISS 1550VP field emission SEM and a JEOL 8200 electron microprobe with solid-state BSE detectors. Quantitative elemental microanalyses (6) were carried out using the JEOL 8200 electron microprobe operated at 10 kV (for smaller interaction volume) and 5 nA in focused beam mode. Analyses were processed with the CITZAF correction procedure (Armstrong 1995) using the Probe for EPMA program from Probe Software, Inc. On-peak interference of V*K*α by Ti*K*β was corrected using the Probe for EPMA. Analytical results are given in Table 1. No other elements with atomic number greater than 4 were detected by WDS scans. The empirical formula (based on 12 oxygen atoms *pfu*) of type hutcheonite is $Ca_{2.99}(Ti^{4+}_{1.53}Mg_{0.25}Al_{0.17}Fe^{2+}_{0.05}V^{3+}_{0.03})(Si_{1.68}Al_{1.32})O_{12}$. According to the newly-approved nomenclature on the garnet supergroup (Grew et al. 2013), this Ti-rich silicate is a new garnet, giving 66% schorlomite charge arrangement, 22% morimotoite charge arrangement, and 12% grossular charge arrangement. Thus, this garnet belongs to the schorlomite group with $Al^{3+} > Fe^{3+}$ at Z. The general formula is $Ca_3(Ti,Mg,Al)_2(Si,Al)_3O_{12}$. The

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end-member formula is $Ca_3Ti_2(SiAl_2)O_{12}$, which requires SiO_2 12.3, TiO_2 32.6, Al_2O_3 20.8, CaO 34.3, total 100.0 wt%.

A potential terrestrial Al analogue of schorlomite has a formula of $(Ca_{2.869}Mg_{0.118}Na_{0.008}Mn_{0.004}Y_{0.001})(Ti_{0.856}Zr_{0.546}Fe^{2+}_{0.212}Mg_{0.202}Fe^{3+}_{0.179}Cr_{0.003})$ $(Si_{2.021}Al_{0.637}Fe^{3+}_{0.342})O_{12}$ (recalculated from Koritnig et al. 1978), which corresponds to 49.0% schorlomite charge arrangement, 41.6% moromotoite charge arrangement, 9.1% grossular charge arrangement and 0.35% other, i.e., a significantly lower proportion of the schorlomite charge arrangement than in the type hutcheonite, which has a much higher Ti and Al content, and thus much closer to the end-member formula in composition.

CRYSTALLOGRAPHY

Conventional X-ray studies could not be carried out because of the small crystal size. Single-crystal electron backscatter diffraction (EBSD) analyses at a sub-micrometer scale were performed using an HKL EBSD system on a ZEISS 1550VP SEM, operated at 20 kV and 6 nA in focused beam mode with a 70° tilted stage and in a variable pressure mode (25 Pa) (Ma and Rossman 2008a, 2009a). The EBSD system was calibrated using a single-crystal silicon standard. The structure was determined and cell constants were obtained by matching the experimental EBSD patterns with structures of grossular, schorlomite, kimzeyite, eringaite, andradite and morimotoite.

The EBSD patterns can be indexed nicely by the *Ia-3d* garnet structure and give the best fit using the grossular structure from Lager et al. (1987) (Fig. 4), with a mean angular deviation of 0.35°. The cell parameters are taken directly from the data of the matching phase in Lager et al. (1987). Cubic Space group: *Ia-3d*, a = 11.843 Å, V = 1661.06 Å^3, Z = 8.

The X-ray powder-diffraction data (in Å for Cu$K\alpha1$, Bragg-Brentano geometry) are calculated from the cell parameters of Lager et al. (1987) with the empirical formula from this study, using Powder Cell version 2.4. The strongest calculated lines are [d in Å, intensity, I, scaled to 100 for the most intense peak, (*h k l*)] [2.648, 100, (*4 2 0*)], [1.583, 63, (*6 4 2*)], [2.961, 54, (*4 0 0*)], [2.417, 41, (*4 2 2*)], [0.806, 30, (*14 4 2*)], [1.642, 27, (*6 4 0*)], [1.292, 18, (*8 4 2*)], and [1.081, 16, (*10 4 2*)].

ORIGIN AND SIGNIFICANCE

Hutcheonite $Ca_3Ti^{4+}{}_2(SiAl_2)O_{12}$ is the Al-analog of schorlomite $Ca_3Ti^{4+}{}_2(SiFe^{3+}{}_2)O_{12}$, and the Ti analog of kimzeyite $Ca_3Zr^{4+}{}_2(SiAl_2)O_{12}$ or irinarassite $Ca_3Sn^{4+}{}_2(SiAl_2)O_{12}$. It is a new member of the schorlomite group in the garnet supergroup (Grew et al. 2013).

Hutcheonite is found only in alteration regions of the Allende CAIs, in close association with secondary monticellite, grossular, and wadalite (Figs. 1–3). These minerals resulted from *in situ* alteration of the Allende CAIs during fluid-assisted thermal metamorphism of the CV chondrite parent asteroid ~3 Myr after CAI formation (Brearley and Krot 2012). Based on these observations, we infer that hutcheonite is also a secondary alteration phase, formed by iron-alkali-halogen metasomatic alteration of the primary melilite, perovskite, and Ti,Al-diopside in the CAI on the Allende parent asteroid. The secondary origin of hutcheonite can be tested by *in situ* aluminum-magnesium and oxygen-isotope measurements. *Egg-3* experienced an open-system post-crystallization alteration that resulted in addition of Si, Na, Cl, and Fe, and loss of Ca.

Primary Ti-rich minerals (i.e., refractory phases) identified in the Allende CAIs include perovskite $CaTiO_3$, Ti,Al-diopside $Ca(Mg,Ti)(Si,Al)_2O_6$, tazheranite $(Zr,Ti,Ca,Y)O_{1.75}$ (Ma and Rossman 2008b), tistarite Ti_2O_3(Ma and Rossman 2009a), rutile TiO_2 (Ma et al. 2009), davisite $Ca(Sc,Ti,Mg)AlSiO_6$ (Ma and Rossman 2009b), grossmanite $CaTiAlSiO_6$ (Ma and Rossman 2009c), panguite $(Ti,Sc,Al,Mg,Zr,Ca,\square)_2O_3$ (Ma et al. 2012), kangite $(Sc,Ti,Al,Zr,Mg,Ca,\square)_2O_3$ (Ma et al. 2013) and paqueite $Ca_3TiSi_2(Al,Ti,Si)_3O_{14}$ (Paque et al. 1994; Ma 2013). However, hutcheonite and Ti,Al-diopside are the only secondary Ti-rich phases identified so far. Secondary Ti,Al-diopside, $(Ca,Na)(Mg,Al,Ti)(Si,Al)_2O_6$ with ~8 wt% TiO_2, was observed to occur with dmisteinbergite (hexagonal $CaAl_2Si_2O_8$) and grossular in several alteration areas in an Allende CAI in section MQM 866 (Fig. 5). Formation of the secondary Ti-rich minerals (hutcheonite and Ti,Al-diopside) during the metasomatic alteration of the Allende CAIs suggests some mobility of Ti during the alteration.

To date, six garnet minerals have been found in meteorites, as listed in Table 2. Hutcheonite is the sixth garnet reported in a meteorite, joining grossular and andradite as alteration products in CAIs. Pyrope in eclogitic clasts from the NWA 801 CR2 meteorite likely formed by metamorphic process at high pressure conditions in a planet-sized body (Kimura et al. 2013), whereas majorite in shock veins from chondrites formed by high-pressure shock process during impact events on asteroidal bodies (e.g., Chen et al. 1996). Meteoritic eringaite, $Ca_3(Sc,Y,Ti)_2Si_3O_{12}$, an ultrarefractory Sc-rich silicate identified in a cluster of CAI fragments from the Vigarano CV3 meteorite, is probably the first garnet formed in the solar system (Ma 2012).

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Table 1. Analytical data for type hutcheonite.

Constituent*	wt%	Range	SD	Probe Standard
SiO_2	20.9	20.4-21.2	0.3	anorthite
TiO_2	25.3	25.0-26.0	0.4	TiO_2
Al_2O_3	15.7	15.3-15.9	0.2	anorthite
CaO	34.6	34.3-34.9	0.2	grossular
MgO	2.1	1.9-2.3	0.2	forsterite
FeO	0.7	0.5-1.0	0.2	fayalite
V_2O_3	0.5	0.3-0.6	0.1	V_2O_5
Total	99.8			

*Average of 6 point analyses.

Table 2. Garnet minerals in meteorites.

Mineral Name	*X*	*Y*	*Z*	O	Type	Reference
grossular	Ca_3	Al_2	Si_3	O_{12}	alteration	e.g. Fuchs 1974
andradite	Ca_3	Fe_2	Si_3	O_{12}	alteration	e.g. Fuchs 1971
hutcheonite	Ca_3	Ti_2	$SiAl_2$	O_{12}	alteration	This study
pyrope	Mg_3	Al_2	Si_3	O_{12}	metamorphic	Kimura et al. 2013
majorite	Mg_3	SiMg	Si_3	O_{12}	high pressure	e.g. Chen et al. 1996
eringaite	Ca_3	Sc_2	Si_3	O_{12}	ultrarefractory	Ma 2012

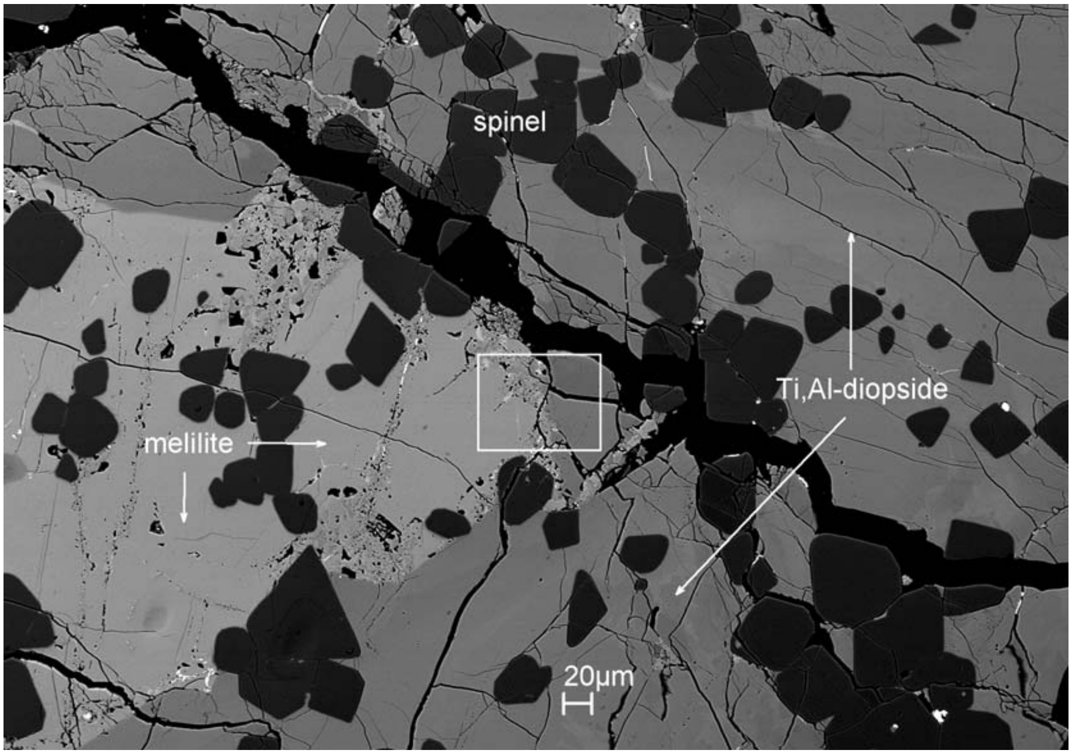


Figure 1. BSE image showing part of the Type B1 CAI *Egg-3* in MQM803. The location of hutcheonite is enclosed by a rectangle box.

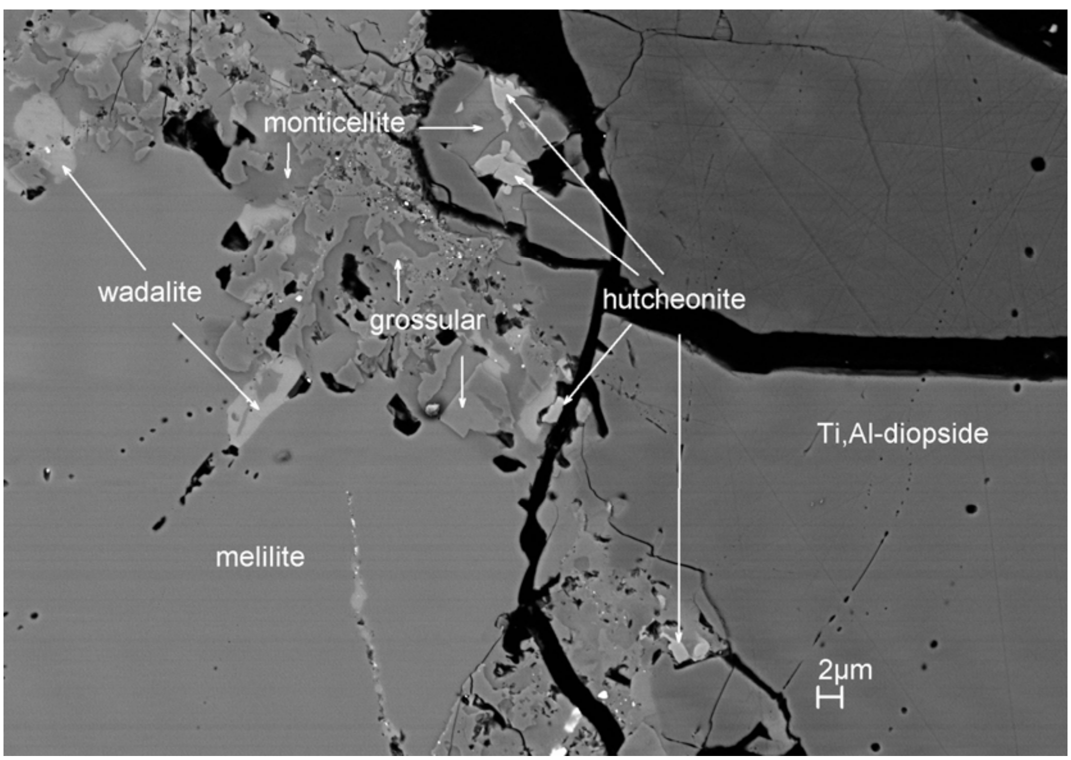
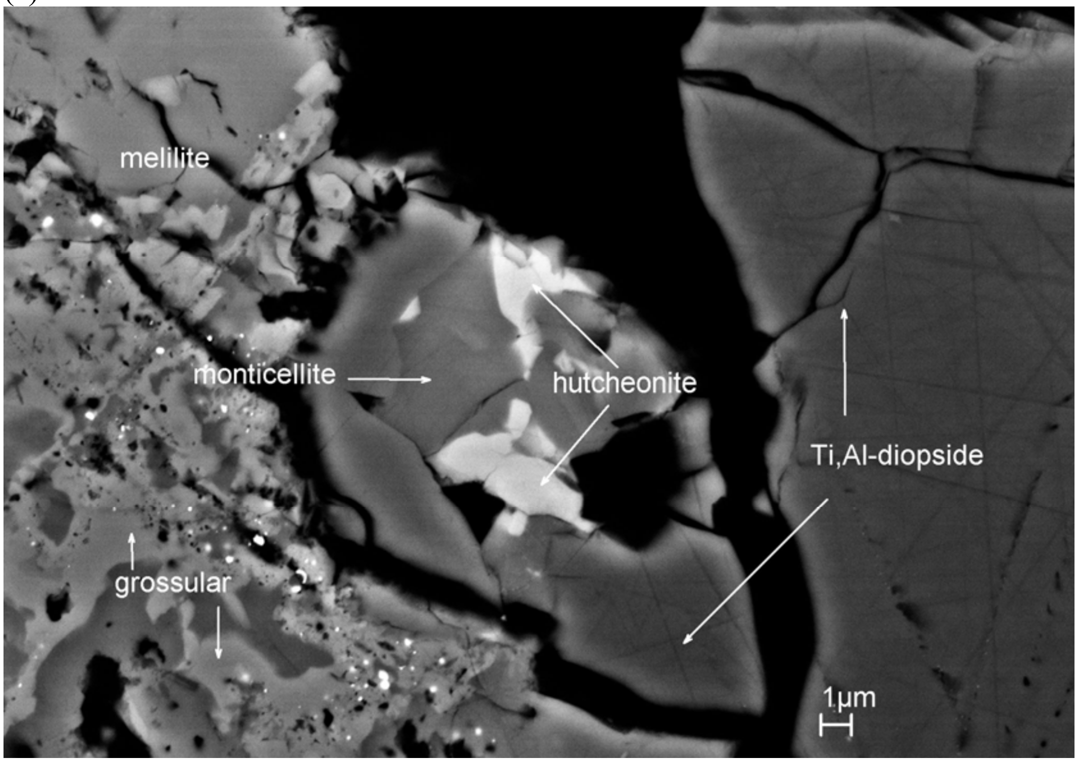


Figure 2. Enlarged BSE image revealing secondary hutcheonite, monticellite, grossular and wadalite in the alteration area between primary melilite and Ti,Al-diopside.

(a)



(b)

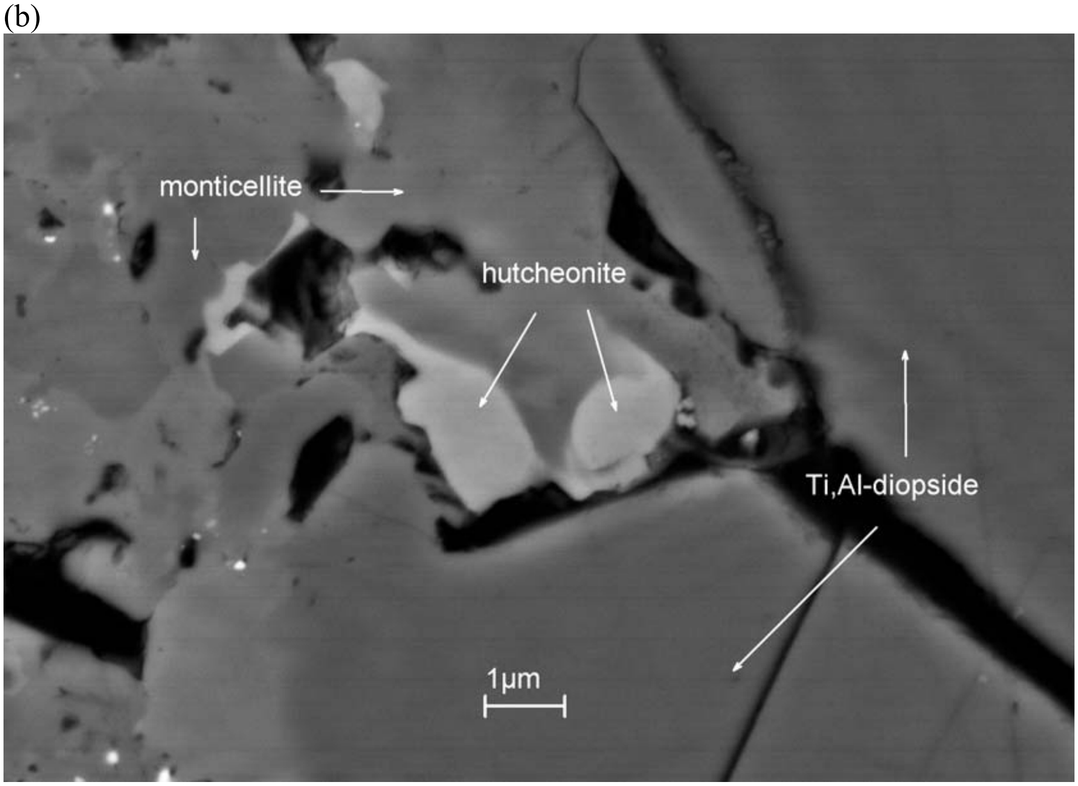


Figure 3. Further enlarge BSE images showing type hutcheonite.

(a) (b)

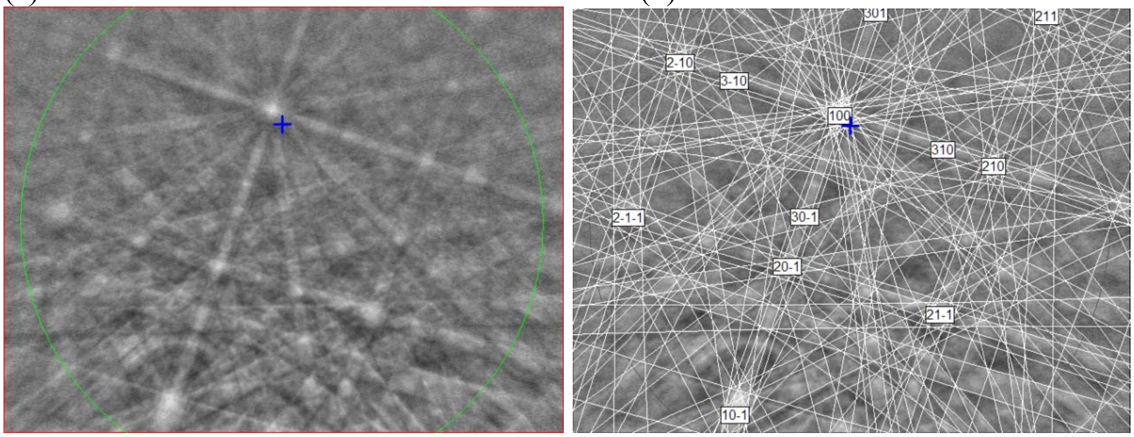
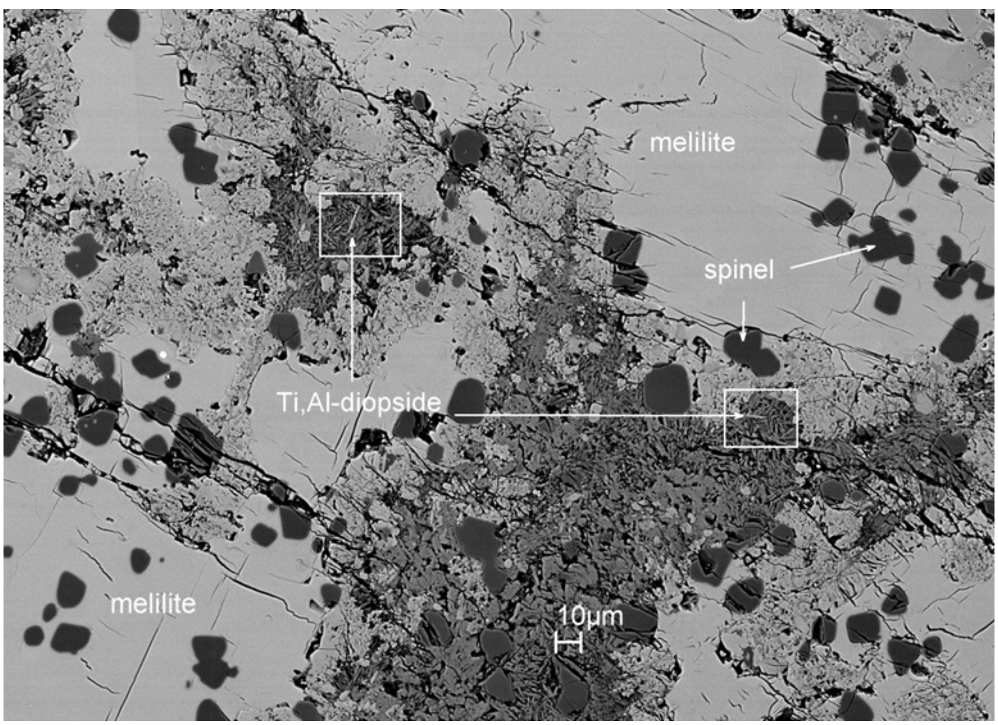
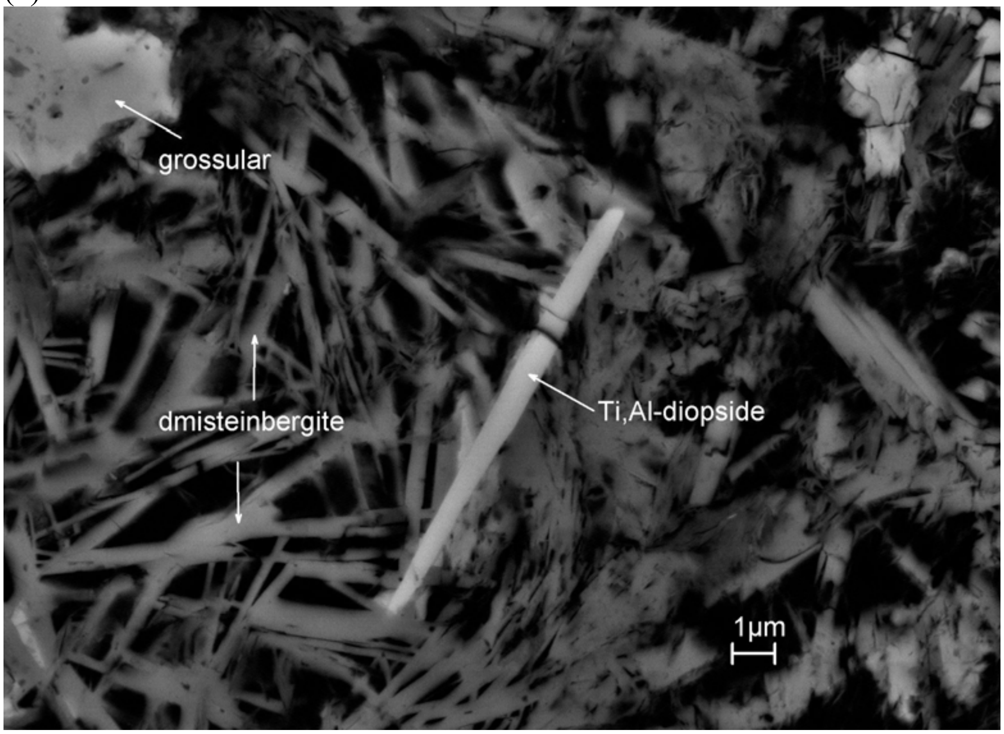


Figure 4. (a) EBSD pattern of the hutcheonite crystal in Fig. 3b, and (b) the pattern indexed with the *Ia-3d* garnet structure.

Figure 5. (a)



(b)



(c)

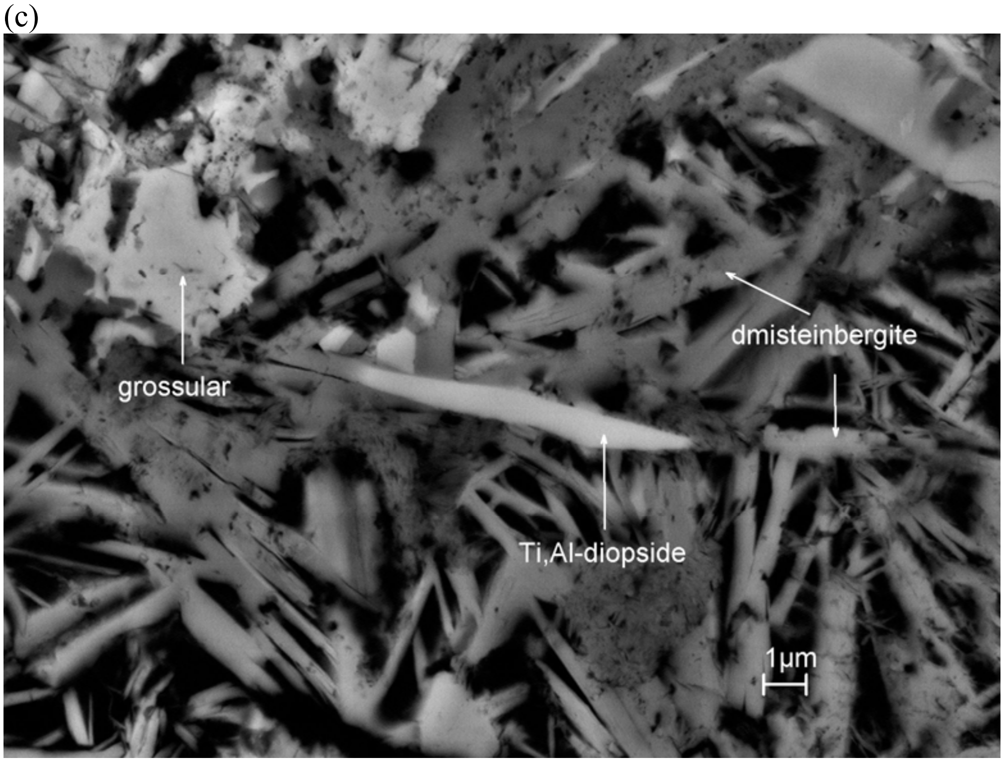


Figure 5. BSE images revealing secondary Ti,Al-diopside, dmisteinbergite and grossular in alteration areas in the Allende CAI in section MQM866.