DOI: https://doi.org/10.2138/am-2018-6505

Revision 2

Adrianite, $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$, a new Cl-rich silicate mineral from the Allende meteorite: An alteration phase in a Ca-Al-rich inclusion

Chi Ma[1,*] and Alexander N. Krot[2]

[1]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA

[2]Hawai‘i Institute of Geophysics and Planetology, University of Hawai‘i at Mānoa, Honolulu, Hawai‘i 96822, USA

ABSTRACT

Adrianite (IMA 2014-028), $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$, is a new Cl-rich silicate mineral and a Si, Mg analog of wadalite. It occurs with monticellite, grossular, wadalite and hutcheonite in altered areas along some veins 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 CV3 carbonaceous chondrite. The mean chemical composition of type adrianite by electron probe microanalysis is (wt%) CaO 41.5, SiO_2 27.5, Al_2O_3 12.4, MgO 7.3, Na_2O 0.41, Cl 13.0, O=Cl -2.94, total 99.2, giving rise to an empirical formula of $(Ca_{11.69}Na_{0.21})(Al_{3.85}Mg_{2.88}Si_{7.23})O_{32}Cl_{5.80}$. The end-member formula is $Ca_{12}(Mg_5Si_9)O_{32}Cl_6$. Adrianite has the $I\bar{4}3d$ wadalite structure with a = 11.981 Å, V = 1719.8 Å^3, and Z = 2, as revealed by electron back-scatter diffraction. The calculated density using the measured composition is 3.03 g/cm^3. Adrianite is a new secondary mineral in Allende, apparently formed by alkali-halogen metasomatic alteration of primary CAI minerals such as melilite, anorthite, perovskite, and Ti,Al-diopside on the CV chondrite parent asteroid. Formation of secondary Cl-rich minerals sodalite, adrianite, and wadalite during metasomatic alteration of the Allende CAIs suggests that the metasomatic fluids had Cl-rich compositions. The mineral name is in honor of Adrian J. Brearley, mineralogist at the University of

New Mexico, USA, in recognition of his many contributions to the understanding of secondary mineralization in chondritic meteorites.

Keywords: adrianite, $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$, new mineral, wadalite group, alteration mineral, Ca-Al-rich inclusion, Allende meteorite, carbonaceous chondrite

----

*E-mail: chi@gps.caltech.edu

INTRODUCTION

During a nanomineralogy investigation of the Allende meteorite, a new Cl-rich silicate, $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$ with the $I\bar{4}3d$ wadalite structure, named “adrianite”, was identified in 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. Much work has been done on *Egg-3* (e.g., Meeker et al. 1983), which 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 composition and structure of adrianite. Synthetic $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$, $Ca_{12}(Al_2Mg_4Si_8)O_{32}Cl_6$, or $Ca_{12}(Mg_5Si_9)O_{32}Cl_6$ have not been reported to date. We describe here the first occurrence of $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$ in a meteorite, as a new alteration mineral 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). Preliminary results of this work are given by Ma and Krot (2014b).

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 2014-028) (Ma and Krot 2014a). The mineral name is in honor of Adrian J. Brearley (born 1958), mineralogist and cosmochemist at the University of New Mexico, in recognition of his many contributions to meteorite mineralogy. He is one of the leading authorities on alteration mineralogy studies of chondritic meteorites. The holotype 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. This section also hosts holotype hutcheonite (IMA 2013-029; Ma and Krot 2014c).

OCCURRENCE AND ASSOCIATED MINERALS

Egg-3 is a coarse-grained igneous Type B1 CAI with a core composed of normally-zoned melilite ($Åk_{46–76}$) and Ti,Al-diopside (in wt.%: 1.9−11.5 TiO_2, 17.2−21.7 Al_2O_3), nearly pure anorthite and Mg-spinel, and a mantle composed of gehlenitic melilite ($Åk_{14–34}$) poikilitically enclosing rounded inclusions of Ti,Al-diopside (in wt.%: 10.3−16.4 TiO_2, 17.8−20.3 Al_2O_3) and spinel (Fig. 1). The coarser spinel grains form a nearly continuous layer in the middle of the melilite mantle. The CAI is surrounded by several rims (from inside outward) (1) a multilayered Wark-Lovering rim (Wark and Lovering 1976) made of melilite+perovskite, Ti,Al-diopside, and forsterite layers, (2) a forsterite-rich accretionary rim (Krot et al. 2001) composed of forsterite overgrown by secondary ferroan olivine, (3) a fine-grained matrix-like rim largely composed of ferroan olivine and nepheline, and (4) a discontinuous layer of salite-hedenbergite pyroxenes and andradite.

The CAI experienced ion-alkali-halogen metasomatic alteration that largely affected its primary melilite and resulted in formation of diverse secondary minerals depending on the melilite composition (Brearley and Krot 2012). Gehlenite-rich melilite of the Wark-Lovering rim is almost completely replaced by sodalite, nepheline, and Na-bearing (up to 1 wt% Na_2O) plagioclase; grossular is minor (Figs. 2a, b). Spinel in the Wark-Lovering rim is enriched in FeO (up to 10 wt.%). Gehlenite-rich melilite in the mantle is crosscut by grossular − Na-bearing plagioclase veins (Figs. 2b, c). The plagioclase/grossular ratio in veins decreases towards the CAI core. Åkermanite-rich melilite in the core is largely replaced by grossular, monticellite, Ti-free Al-diopside, and wollastonite; secondary forsterite, kushiroite, wadalite, hutcheonite, and adrianite are minor (Figs. 2d, e). The core anorthite experienced relatively minor alteration; it is crosscut by veins of grossular, Na-rich melilite (up to 4.7 wt% Na_2O), kushiroite, and celsian ($BaAl_2Si_2O_8$) (Figs. 2e, f). A trace amount of Ni-Fe-rich metal is present in the CAI core.

Adrianite occurs in contact with monticellite and grossular, plus nearby wadalite and hutcheonite in alteration areas along some cracks between primary melilite, spinel and Ti,Al-diopside in the core area of the CAI (Figs. 3−5). Hutcheonite ($Ca_3Ti_2(SiAl_2)O_{12}$) is a newly-found garnet mineral (Ma and Krot 2014c).

X-ray elemental mapping reveals a zoned distribution of Na- and/or Cl-rich secondary minerals: nepheline and sodalite occur largely in the peripheral part of the CAI, whereas wadalite and adrianite are found exclusive in its core; the melilite mantle virtually lack Na- and Cl-rich secondary minerals (Fig. 1).

APPEARANCE, PHYSICAL, AND OPTICAL PROPERTIES

Adrianite occurs as small, irregular, single crystals, 2−6 µm in size (Figs. 3−5), which are the holotype material. Color, luster, streak, hardness, tenacity, cleavage, fracture, density, and optical properties could not be determined because of the small grain size. Adrianite is non-cathodoluminescent under the electron beam in an SEM. The calculated density is 3.03 g/cm^3 using the empirical formula.

CHEMICAL COMPOSITION

Backscattered electron (BSE) images were obtained using a ZEISS 1550VP field emission SEM and a JEOL 8200 electron microprobe with AsB (angle selective backscatter) and solid-state BSE detectors, respectively. Quantitative elemental microanalyses (3) 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. 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 32 oxygen atoms *pfu*) of type adrianite is $(Ca_{11.69}Na_{0.21})(Al_{3.85}Mg_{2.88}Si_{7.23})O_{32}Cl_{5.80}$. This Cl-rich silicate is a new wadalite group mineral with $Si^{4+} > Al^{3+}$ at tetrahedral sites in the structure. The general formula is $Ca_{12}(Si,Al,Mg)_{14}O_{32}Cl_6$. The ideal formula of the holotype material is $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$. The end-member formula is likely $Ca_{12}(Mg_5Si_9)O_{32}Cl_6$, which requires SiO_2 34.23, MgO 12.76, CaO 42.59, Cl 13.46, O = Cl -3.04, total 100.0 wt%. Associated wadalite has an empirical formula of $(Ca_{11.58}Na_{0.09})(Al_{7.42}Mg_{1.29}Si_{5.39})O_{32}Cl_{5.66.}$ Nearby primary melilite has an empirical formula of $Ca_{2.00}(Mg_{0.51}Al_{0.45})(Si_{1.55}Al_{0.45})O_7$, and Ti,Al-diopside shows an empirical formula of $Ca_{1.00}(Mg_{0.52}Al_{0.25}Ti_{0.18})(Si_{1.45}Al_{0.55})O_6$ with ~18 wt% Al_2O_3 and ~7 wt% TiO_2.

CRYSTALLOGRAPHY

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 2008, 2009). 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 wadalite, grossular, and mayenite.

The EBSD patterns can be indexed nicely by the $I\bar{4}3d$ wadalite structure and give a best fit using the wadalite structure from Feng et al. (1988) (Fig. 6), with a mean angular deviation of 0.31º, showing a = 11.981 Å, V = 1719.8 Å^3, and Z = 2.

The X-ray powder-diffraction data (in Å for Cu$K\alpha1$, Bragg-Brentano geometry) are calculated from the cell parameters and the atomic coordinates of Feng et al. (1988) 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*)] [2.679, 100, (*4 2 0*)], [2.446, 36, (*4 2 2*)], [2.995, 32, (*4 0 0*)], [1.661, 28, (*6 4 0*)], [1.601, 28, (*6 4 2*)], [4.891, 14, (*2 1 1*)], [2.187, 14, (*5 2 1*)], and [1.729, 14, (*4 4 4*)].

ORIGIN, SIGNIFICANCE AND IMPLICATIONS

Adrianite, $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$, is the Si, Mg analogue of wadalite $Ca_{12}(Al_{10}Si_4)O_{32}Cl_6$. It is a new member of the wadalite group in the manyenite supergroup. Its end-member may be $Ca_{12}(Mg_5Si_9)O_{32}Cl_6$.

Adrianite is found only in altered regions of the Allende CAIs, in close association with secondary monticellite, grossular, hutcheonite, and wadalite (Figs. 3−5). Mineralogical observations, thermodynamic analysis, and oxygen and ^{26}Al-^{26}Mg isotope systematics of grossular, monticellite, and wollastonite in CV chondrites indicate that these minerals resulted from *in situ* alteration of the Allende CAIs during fluid-assisted thermal metamorphism of the CV chondrite parent asteroid below 600°C, ~3–4 Myr after CAI formation (Krot et al. 2007; Brearley and Krot 2012). Based on these observations, we infer that adrianite is also a secondary alteration product, formed by iron-alkali-halogen metasomatic alteration of the primary melilite, perovskite, and Ti,Al-diopside in the CAI on the Allende parent asteroid. *Egg-3* experienced

This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2018-6505

open-system, post-crystallization alteration that resulted in addition of Si, Na, Cl, and Fe, and loss of Ca (Fig. 1); Al, Ti, and Mg were also mobile during the alteration. One possible reaction to account for adrianite formation in *Egg-3*, based on simplified or end-member formulas, may be expressed as:

$$3Ca_2(Mg_{0.5}Al_{0.5})(Si_{1.5}Al_{0.5})O_7(\text{melilite}) + Ca_{1.00}(Mg_{0.5}Al_{0.25}Ti_{0.25})(Si_{1.5}Al_{0.5})O_6(\text{Al,Ti-diopside}) + Cl(aq) + 6.12H_2O(l) = 0.17Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6(\text{adrianite}) + 0.13Ca_3Ti_2(SiAl_2)O_{12}(\text{hutcheonite}) + 1.5CaMgSiO_4(\text{monticellite}) + 0.88Ca_3Al_2Si_3O_{12}(\text{grossular}) + 0.5CaAl_2SiO_6(\text{kushiroite}) + 1.39Ca(aq) + 0.05Al(aq) + 0.04SiO_2(aq) + 6.12H_2(g),$$

where grossular, monticellite and kushiroite (CaTs, Ti-free Al-rich pyroxene) are among the common secondary minerals, and melilite and Al,Ti-diopside are the major primary minerals that were altered.

Secondary Cl-rich minerals identified in CAIs now include sodalite, chlormayenite (previously known as “brearleyite”; Ma et al. 2011), wadalite, and adrianite. Each and every new mineral identified in meteorites provide new information on forming conditions. Adrianite is one of six new secondary minerals discovered in Allende CAIs, helping to reveal alteration processes on the parent body.

ACKNOWLEDGMENTS

SEM, EBSD and EPMA were carried out at the Geological and Planetary Science Division Analytical Facility, Caltech, which is supported in part by NSF grants EAR-0318518 and DMR-0080065. This work was also supported by NASA grant NNX12AJ01G. We thank Mike Zolensky, Makoto Kimura, and associate editor Steve Simon for constructive reviews.

REFERENCES CITED

Armstrong , J.T. (1995) CITZAF: A package of correction programs for the quantitative electron beam X-ray analysis of thick polished materials, thin films, and particles. Microbeam Analysis, 4, 177−200.

Brearley, A.J. and Krot, A.N. (2012) Metasomatism in the early solar system: The record from chondritic meteorites. In Metasomatism and the Chemical Transformation of Rock – Lecture Notes in Earth System Sciences, 659−789.

DOI: https://doi.org/10.2138/am-2018-6505

Feng, Q.L., Glasser, F.P., Howie, R.A., and Lachowski, E.E. (1988) Chlorosilicate with the $12CaO{\cdot}7Al_2O_3$ structure and its relationship to garnet. Acta Crystallographica, C44, 589–592.

Krot, A.N., Ulyanov, A.A., Meibom, A., and Keil, K. (2001) Forsterite-rich accretionary rims around Ca, Al-rich inclusions from the reduced CV3 chondrite Efremovka. Meteoritics & Planetary Sciences, 36, 611−628.

Krot, A.N., Yurimoto, H., Hutcheon, I.D., Libourel, G., Chaussidon, M., Petaev, M.I., MacPherson, G.J., Paque-Heather, J., and Wark., D. (2007) Anorthite-rich, igneous (Type C) Ca,Al-rich inclusions from the CV carbonaceous chondrite Allende: Evidence for multistage formation history. Geochimica et Cosmochimica Acta 71, 4342−4364.

Ma, C. and Krot, A.N. (2014a) Adrianite, IMA 2014-028. CNMNC Newsletter No. 21, August 2014, page 801. Mineralogical Magazine, 78, 797−804.

Ma, C. and Krot, A.N. (2014b) Discovery of a new Cl-rich silicate mineral, $Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$: an alteration phase in Allende. 77th Annual Meteoritical Society Meeting, Abstract #5432.

Ma, C. and Krot, A.N. (2014c) 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. American Mineralogist, 99, 667−670.

Ma, C. and Rossman, G.R. (2008) Barioperovskite, $BaTiO_3$, a new mineral from the Benitoite Mine, California. American Mineralogist, 93, 154−157.

Ma, C. and Rossman, G.R. (2009) Tistarite, Ti_2O_3, a new refractory mineral from the Allende meteorite. American Mineralogist, 94, 841−844.

Ma, C., Connolly, H.C., Beckett, J.R., Tschauner, O., Rossman, G.R., Kampf, A.R., Zega, T.J., Sweeney Smith, S.A., and Schrader, D.L. (2011) Brearleyite, $Ca_{12}Al_{14}O_{32}Cl_2$, a new alteration mineral from the NWA 1934 meteorite. American Mineralogist, 96, 1199−1206.

Meeker, G.P., G.J Wasserburg, G.J., and Armstrong, J.T. (1983) Replacement textures in CAI and implications regarding planetary metamorphism. Geochimica et Cosmochimica Acta, 47, 707−721.

Wark, D.A. and Lovering, J.F. (1976) Marker events in the early evolution of the solar system: Evidence from rims on Ca-Al-rich inclusions in carbonaceous chondrites meteorites. Proceedings of the Lunar and Planetary Science Conference, 8, 95−112.

Wasserburg G.J., Wimpenny, J., and Yin, Q.-Z. (2012) Mg isotopic heterogeneity, Al-Mg isochrons, and canonical $^{26}Al/^{27}Al$ in the early solar system. Meteoritics & Planetary Sciences, 47, 1980–1997.

DOI: https://doi.org/10.2138/am-2018-6505

Table 1. EPMA data for type adrianite and nearby wadalite in *Egg-3*.

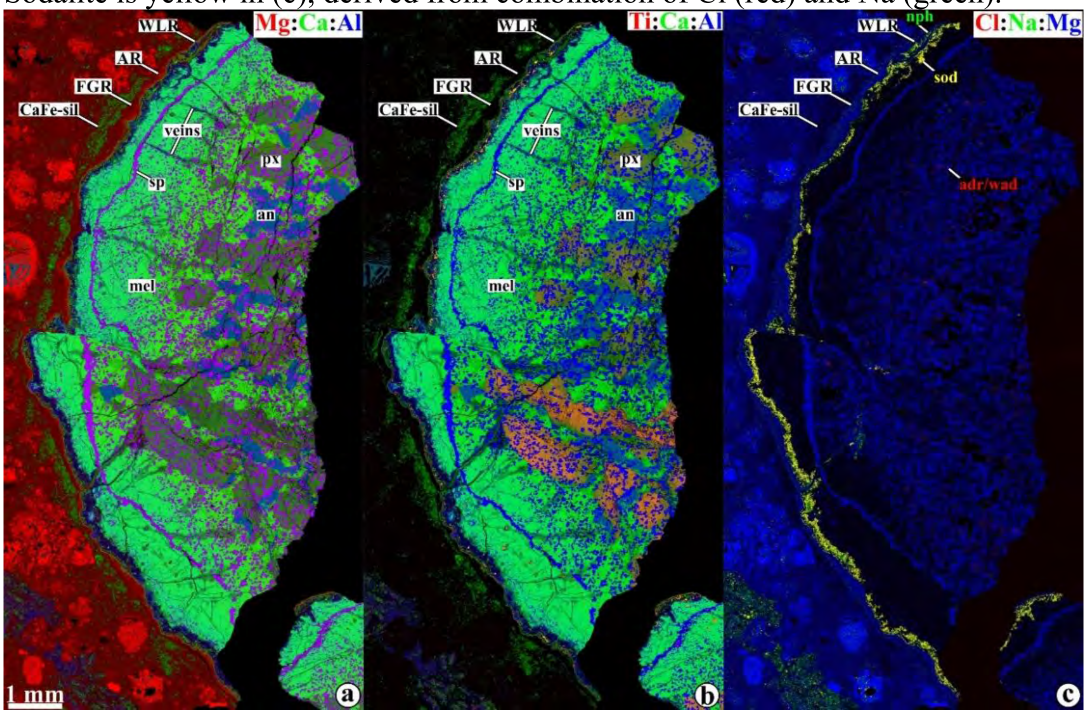
Constituent (wt%)[a]	adrianite	wadalite	Probe Standard
	n=3[b]	n=3	
SiO_2	27.5(3)[c]	20.6(1)	grossular
Al_2O_3	12.4(2)	24.0(5)	grossular
MgO	7.3(2)	3.3(4)	forsterite
CaO	41.5(4)	41.2(2)	grossular
Na_2O	0.41(3)	0.2(1)	albite
Cl	13.0(3)	12.73(3)	sodalite
-O	2.94(7)	2.87(1)	
Total	99.2	99.2	

[a] Detection limit at 99% confidence: 0.07 wt% Si, 0.07 wt% Al, 0.03 wt% Mg, 0.04 wt% Ca, 0.05 wt% Na, 0.04 wt% Cl.

[b] Number of point analyses.

[c] Standard deviation in bracket.

Figure 1. Combined x-ray elemental maps in (a) Mg (red), Ca (green) and Al (blue), (b) Ti (red), Ca (green) and Al (blue), (c) Cl (red), Na (green) and Mg (blue), and x-ray elemental maps in (d) Mg, (e) Si, and (f) Ca of the Allende Type B1 CAI *Egg-3*. The CAI experienced open-system alteration that resulted in addition of Si, Na, Cl, and Fe, and loss of Ca. adr = adrianite; an = anorthite; AR = forsterite-rich accretionary rim; CaFe-sil = layer of salite-hedenbergite pyroxenes and andradite; FGR = fine-grained matrix-like rim; mel = melilite; nph = nepheline; px = Ti,Al-diopside; sod = sodalite; sp = spinel; wad = wadalite; WLR = Wark-Lovering rim. Sodalite is yellow in (c), derived from combination of Cl (red) and Na (green).



This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2018-6505

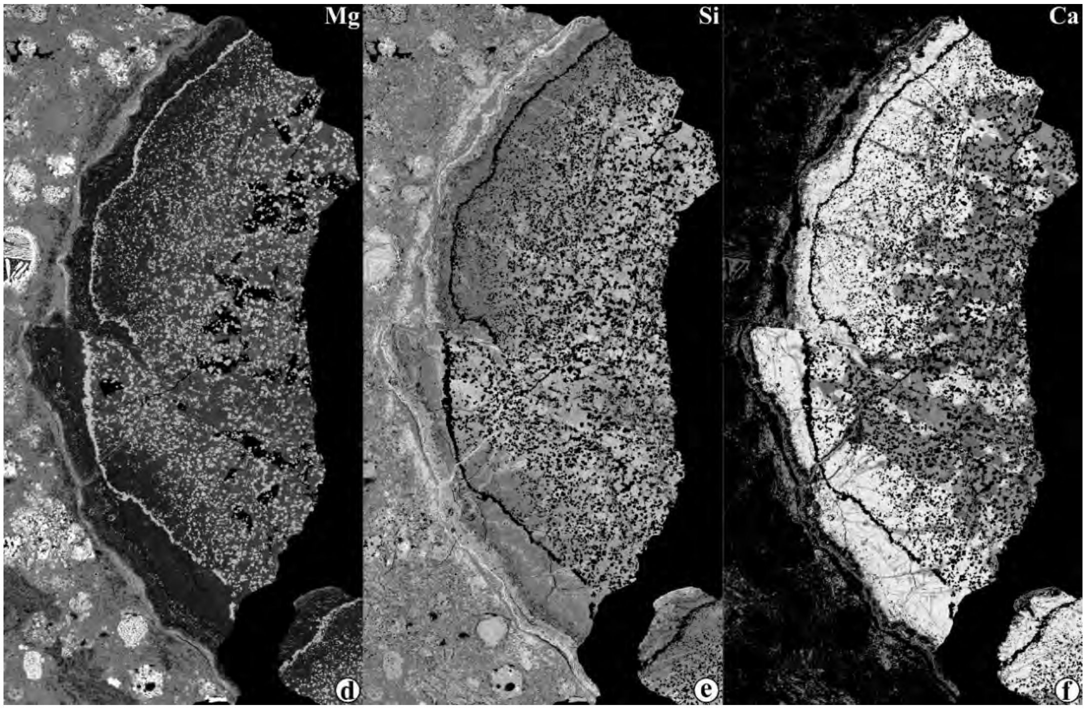
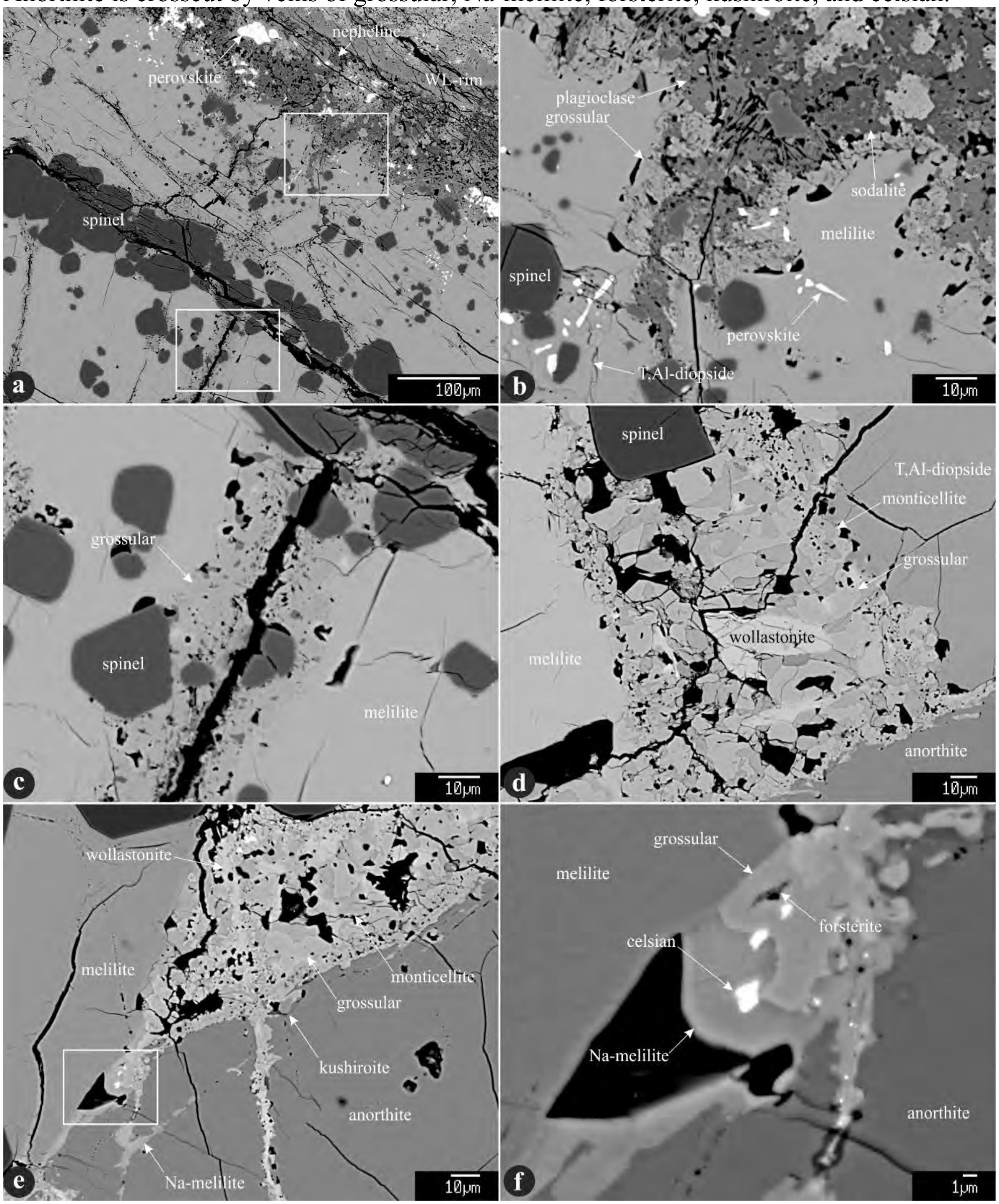
238 

Figure 2. SEM BSE images showing secondary mineralization in different parts of *Egg-3*. Regions outlined in “a” and “e” are shown in detail in “b, c” and “f”, respectively. (a–c) Gehlenitic melilite near the Wark-Lovering (WL) rim is replaced by nepheline, sodalite, and Na-bearing plagioclase. Gehlenitic melilite in the mantle is crosscut by plagioclase-grossular veins. The abundance of anorthite in veins decreases towards the CAI core. (d–f) In the CAI core, åkermanitic melilite is replaced by grossular, monticellite, wollastonite, and Ti-free Al-diopside. Anorthite is crosscut by veins of grossular, Na-melilite, forsterite, kushiroite, and celsian.



This is a preprint, the final version is subject to change, of the American Mineralogist (MSA)
Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2018-6505

Figure 3. SEM BSE image showing part of the Type B1 CAI *Egg-3* in MQM803. The location of adrianite is indicated by the box and shown in Fig. 4.

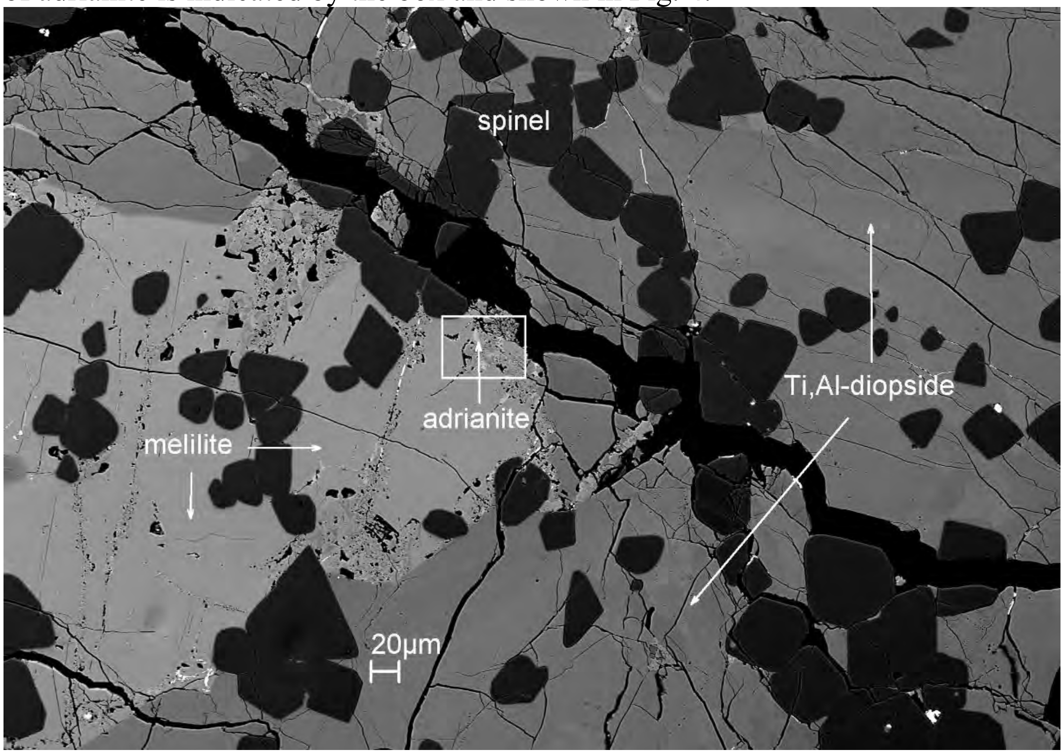
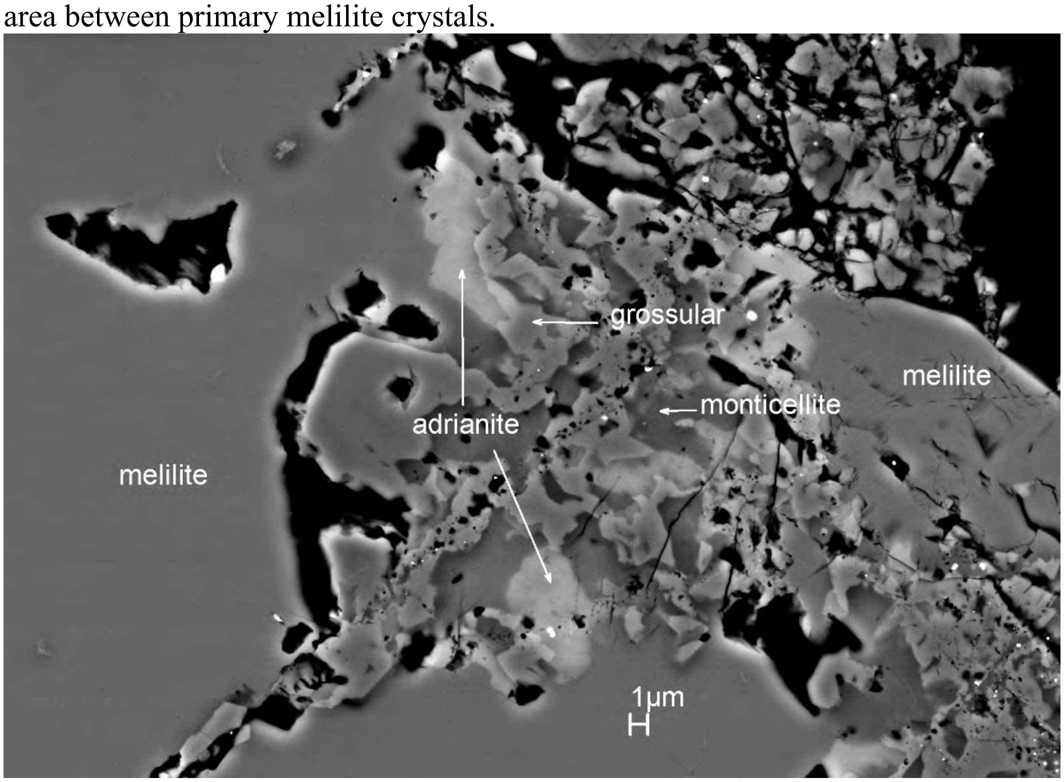


Figure 4. Enlarged BSE image revealing adrianite with grossular and monticellite in the altered area between primary melilite crystals.



DOI: https://doi.org/10.2138/am-2018-6505

Figure 5. BSE image showing adrianite with grossular between melilite and Ti,Al-diopside.

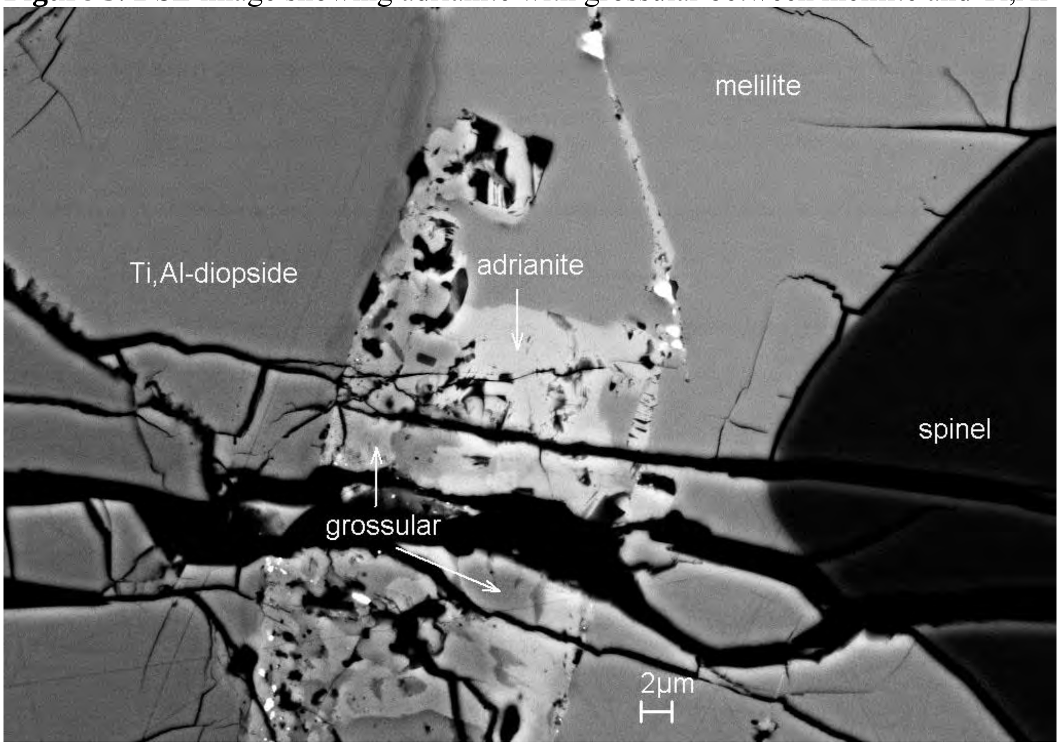


Figure 6. (left) EBSD pattern of the adrianite crystal in Figure 2, and (right) the pattern indexed with the *I-43d* wadalite structure.