

**DISCOVERY OF A NEW CHALCOGENIDE MINERAL, Ni₉Ge₂S₂, IN ALLENDE:
AN ALTERATION PHASE FROM THE EARLY SOLAR SYSTEM.**

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Introduction: The Allende CV3 carbonaceous chondrite, fell in Mexico on February 8, 1969, is the best-studied meteorite in history. More than fifty years after it fell, this space rock continues to be source of new discoveries. Allende has yielded 19 IMA-approved new minerals already since 2007 [e.g., 1-6], including 12 refractory phases and 5 late-stage alteration phases, adding new puzzle pieces to the big picture of nebular and parent body processes in the early solar system. Reported here is the discovery of another new chalcogenide mineral, Ni₉Ge₂S₂, an alteration phase in a Ca-Al-rich inclusion – the latest new mineral from Allende.

During an ongoing nanomineralogy investigation of the Allende meteorite, a new chalcogenide mineral, (Ni,Fe)₉(Ge,Sn)₂(S,Te)₂ with an intergrowth structure in a tetragonal system, was identified in the coarse-grained igneous Type B1 Ca-Al-rich inclusion (CAI) *Egg-3* in section USNM 7929. Field-emission scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), electron back-scatter diffraction (EBSD) and electron probe microanalyzer (EPMA) were used to characterize this mineral and associated phases. Synthetic Ni_{8.24}Ge₂S₂ and Ni₉Sn₂S₂ are well known [7,8]. This natural chalcogenide (Ni,Fe)₉(Ge,Sn)₂(S,Te)₂ (ideally Ni₉Ge₂S₂) from Allende is currently under review by the IMA-CNMNC for approval as a new mineral.

Occurrence, Chemistry, and Crystallography: This chalcogenide phase occurs as irregular crystals, 2–6 μm in size, with Ge-bearing Ni-Fe alloy, millerite, nuwaite, butianite, wollastonite, andradite, grossular and diopside in an alteration region between primary spinel and Al,Ti-diopside in the core area of the CAI in section USNM 7929. *Egg-3* is a Type B1 (with a melilite) FUN (Fractionation and Unidentified Nuclear effects) CAI. Primary melilite with spinel, Al,Ti-diopside and anorthite occupies the mantle-core area with a Wark-Lovering rim composed of Al,Ti-diopside and forsterite. Other secondary minerals in alterations areas in *Egg-3* include monticellite, wadalite, recently found hutcheonite (Ca₃Ti₂(SiAl₂)O₁₂; IMA 2013-029) [2] and adrianite (Ca₁₂(Al₄Mg₃Si₇)O₃₂Cl₆; IMA 2014-028) [3]. Traces of Fe,Ni-rich metal are present in *Egg-3*. The matrix around the CAI consists of Fe-rich olivine, nepheline, diopside-hedenbergite pyroxenes, and minor troilite and pentlandite [2,3].

The chemical composition of this chalcogenide by EPMA (WDS) is (wt%) Ni 68.32, Ge 15.14, S 8.04, Te 3.22, Fe 2.65, Sn 2.03, Co 0.23, sum 99.64, showing an empirical formula (based on 2 atoms of S+Te) of (Ni_{8.43}Fe_{0.34}Co_{0.03})(Ge_{1.51}Sn_{0.12})(S_{1.82}Te_{0.18}). The simplified formula is (Ni,Fe)₉(Ge,Sn)₂(S,Te)₂. The ideal formula is Ni₉Ge₂S₂. The EBSD patterns of this chalcogenide can be indexed only by the *I4/mmm* Ni₉Sn₂S₂-Ni_{8.21}Ge₂S₂-type structure and give a perfect fit to the synthetic Ni_{8.21}Ge₂S₂ cell [7], with a mean angular deviation of 0.27°-0.35°, revealing *a* = 3.58(1) Å, *c* = 24.69(1) Å, *V* = 316(1) Å³, and *Z* = 2. The new chalcogenide mineral (Ni₉Ge₂S₂) has an intergrowth structure, related to nuwaite (Ni₆GeS₂; IMA 2013-018) and butianite (Ni₆SnS₂; IMA 2016-028) [4]. Their crystal structures are assembled from heterometallic Ni-Ge (or Ni-Sn) and Ni-S slabs alternating along the *c*-axis in a tetragonal system [7,8].

Origin and Significance: This chalcogenide Ni₉Ge₂S₂ is the most Ge-rich phase identified so far from the early solar system. Along with nuwaite (Ni₆GeS₂) and butianite (Ni₆SnS₂), this chalcogenide is a late-stage, likely vapor-deposited, alteration product, filling in pores within the alteration region in CAI *Egg-3*. These phases and associated Ge-bearing Ni-Fe alloy are observed only within *Egg-3* and not outside it or at the inclusion-matrix interface, just like type nuwaite and butianite in CAI *ACM-2* [4]. They were derived through a sulfidation process, in which a highly localized, low-temperature Ge-, Sn-, Te-bearing fluid interacted with portions of the host CAIs [4].

References: [1] Ma C. et al. 2012. *American Mineralogist* 97, 1219–1225. [2] Ma C. and Krot A.N. 2014. *American Mineralogist* 99, 667-670. [3] Ma C. and Krot A.N. 2018. *American Mineralogist* 103, 1329–1334. [4] Ma C. and Beckett J.R. 2018. *American Mineralogist* 103, 1918–1924. [5] Ma C. and Beckett J.R. 2021. *Meteoritics & Planetary Science* 56, 96-107. [6] Ma C. et al. 2021. *Meteoritics & Planetary Science* 56, 2265-2272. [7] Isaeva A.A. et al. 2009. *Solid State Sciences* 11, 1071-1076. [8] Baranov A.I. et al. 2003. *Inorganic Chemistry* 42, 6667-6672.