Nuwaite (Ni₆GeS₂) and butianite (Ni₆SnS₂), two new minerals from the Allende meteorite: Alteration products in the early solar system

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ABSTRACT

Nuwaite (Ni₆GeS₂, IMA 2013-018) and butianite (Ni₆SnS₂, IMA 2016-028) are two new chalcogenide minerals, occurring as micrometer-sized crystals with grossular, Na-bearing melilite, heazlewoodite, and Ge-bearing Ni-Fe alloys in veins and as mono-mineralic crack-filling material in igneous diopside in the Type B1 Ca-Al-rich inclusion (CAI) ACM-2 from the Allende CV3 carbonaceous chondrite. The chemical composition of type nuwaite is (wt%) Ni 65.3, S 10.3, Ge 8.2, Te 7.9, Sn 5.1, and Fe 1.7, with a sum of 98.5 and an empirical formula of \((\text{Ni}_{5.95}\text{Fe}_{0.16})(\text{Ge}_{0.66}\text{Sn}_{0.23})(\text{S}_{1.72}\text{Te}_{0.33})\). The simplified formula is \(\text{Ni}_6(\text{Ge},\text{Sn})(\text{S},\text{Te})_2\), leading to an end-member of \(\text{Ni}_6\text{GeS}_2\). The chemical composition of type butianite is (wt%) Ni 62.1, Sn 8.9, Te 10.3, S 8.9, Ge 5.3, Fe 1.3, sum 99.1, giving rise to an empirical formula of \((\text{Ni}_{10.9}\text{Ge}_{0.1})(\text{Sn}_{0.52}\text{Ge}_{0.41})(\text{S}_{1.16}\text{Te}_{0.43})\). Butianite’s simplified formula is \(\text{Ni}_6(\text{Sn},\text{Ge})_2(\text{S},\text{Te})_3\), and the end-member formula is \(\text{Ni}_6\text{SnS}_2\). Both nuwaite and butianite have an \(I4/mmm\) intergrowth structure with \(a = 3.65\ \text{Å}, c = 18.14\ \text{Å}, V = 241.7\ \text{Å}^3\), and \(Z = 2\). Their calculated densities are 7.24 and 7.62 g/cm³, respectively. Nuwaite and butianite are the first known meteoritic minerals with high Ge and Sn concentrations.

Nuwaite and butianite are very late-stage, vapor-deposited, alteration products, filling in pores within preexisting grossular-rich alteration veins and cracks in igneous Al-Ti-diopside. These phases and associated heazlewoodite and Ge-bearing alloys are observed only within the Ca-, Al-rich inclusion (CAI) and not outside it or at the inclusion-matrix interface. As only sections in one half of ACM-2 contain nuwaite/butianite, they were probably derived through a relatively low \(f_{O_2}\)-\(f_{S_2}\) sulfidation process, in which a highly localized, low-temperature Ge-, Sn-bearing fluid interacted with a portion of the host CAI. It is likely that the fluid became relatively more Sn- and Te-enriched with time and that crack fillings post-date vein fillings, possibly due to a late remobilization of vein sulfides.

**Keywords:** Nuwaite, \(\text{Ni}_6\text{GeS}_2\), butianite, \(\text{Ni}_6\text{SnS}_2\), new minerals, Allende meteorite, CV3 carbonaceous chondrite, Ca-Al-rich inclusions

INTRODUCTION

The alteration of Ca-Al-rich inclusions (CAIs) in meteorites is a story of secondary processes during the early evolution of the solar system. New secondary minerals can provide special insight because they sample special environments not encountered by most inclusions (e.g., Ma et al. 2011) or because they respond to aspects of an environment that was encountered by other phases but poorly recorded (e.g., Ma et al. 2014a). In this work, we report two new chalcogenide minerals, nuwaite (\(\text{Ni}_6\text{GeS}_2\)) and butianite (\(\text{Ni}_6\text{SnS}_2\)), which were discovered in alteration veins and filling cracks in pyroxene phenocrysts within the Type B1 CAI ACM-2 from the Allende CV3 chondrite. Nuwaite and butianite are the first minerals observed in meteorites that contain structurally essential Ge (nuwaite) and Sn (butianite). In addition to nuwaite and butianite, ACM-2 is the source of three previously described new minerals, grossmanite (\(\text{CaTi}_3\text{AlSi}_3\text{O}_{10}\)), monipite (\(\text{MoNiP}\)), and majindeite (\(\text{Mg}_2\text{Mo}_3\text{O}_8\)) (Ma and Rossman 2009b; Ma et al. 2014a; Ma and Beckett 2016), two of which (monipite and majindeite) are alteration phases after refractory metals.

Germanium is an unusual element in having variable behavior depending on physical and redox conditions (e.g., Bernstein 1985; Rouxel and Luais 2017), which can sometimes be harnessed to explore the environment. For example, variations in trace Ge as a function of Ni content form the basis for classification and a delineation of fractionation processes within individual groups of iron meteorites (e.g., Scott and Wasson 1975). In terrestrial aqueous systems, Ge commonly co-precipitates in low concentrations with iron oxy(hydroxy)-oxides, opaline silica, or organic material and is sometimes tapped as an environmental tracer (e.g., Bernstein 1985; Bernstein and Waychunas 1987; Froehlich et al. 1985; Kurtz et al. 2002). In hydrothermal systems, Ge (and Sn) are often present in small concentrations in sphalerite, wurtzite, and chalcopyrite (e.g., Johan 1988; Reiser et al. 2011; Frenzel et al. 2014; Evrard et al. 2015). Occasionally, Ge concentrations in a phase are high enough to produce minerals with Ge as a structurally important constituent. In rare examples, minerals with structurally important Ge are even encountered at commercially viable concentrations, the most famous example being in the oxidative alteration zone of a sulfide body at Tsumeb, Namibia (Frondel and Ito 1957; Melcher et al. 2006).

Tin, in the form of Cu-Sn alloys (i.e., bronze), is the technological basis for many early civilizations. Tin mineralization on Earth is most commonly associated with oxides from late-stage granitic liquids and low-sulfide hydrothermal fluids derived from silicic intrusions (e.g., Mlynarczyk and Williams-Jones 2006), but it can also occur in the form of tin sulfides in sulfide bodies,