An experimental study on the formation of niningerite and oldhamite: Implication for the chondrule formation of the EH3 chondrite

Naoya Imae[1,2]
[1]*National Institute of Polar Research,* [2]*SOKEDAI*

Introduction

Enstatite chondrites are thought to be the main building blocks that formed the Earth (e.g., Piani et al., 2020). The origin of E3 chondrites is thus of great interest but not been well constrained (Jacquet et al., 2018). The E chondrites are chemically distinguished from EH (high iron type) and EL (low iron type) chondrites (Weisberg and Kimura, 2012). The EH3 chondrites are mainly characterized by abundant type IB chondrules, mainly composed of clinoenstatites, and metal-sulfide nodules, mainly composed of troilite and kamacite, with highly reduced minerals such as niningerite and oldhamite commonly present in both the main chondrules and nodule components (e.g., Ikeda 1989; Weisberg and Kimura, 2012). These minerals would have formed by sulfidation of silicates based on the textural and thermochemical considerations (Lehner et al., 2013), however, their origin has not been studied in detail experimentally. Based on the hypothesis that these two major components of chondrules and nodules formed simultaneously, a new experimental technique was designed with additional starting materials and a modification for silica glass protection based on the previous pioneering work (Fleet and MacRae, 1987). In the present study, niningerite and oldhamite were successfully synthesized from the sulfidation of magnesian olivine, and Ca-poor and Ca-rich pyroxenes. After the additional runs, the experimental results would be analyzed and applied to the simultaneous formation of chondrules and metal nodules in the EH3 chondrites.

Experiments

Tiny fragments of magnesian olivine and pyroxenes were prepared, olivine (Fa#=8-9 at%, San Carlos), enstatite (Fs#=8-9 at%, Tanzania), and diopside (Sar-e Sang, Afghanistan), with 4C pyrrhotite ($Fe_{0.875}S$, Chihuahua, Mexico). Each was placed in a graphite crucible (Fig. 1). Then, each pair with pyrrhotite was enclosed in an evacuated silica tube (Run#s: SCPo-7, -8 EnPo-1, -2, and DiPo-1). Considering that thermochemical stability shows that niningerite is stable more than ~1200ºC under the pS_2 in the Fe-FeS equilibrium (Fleet and MacRae, 1987), and the reduced condition in the alumina ceramic tube suppresses the crystallization of silica glass to cristobalite (e.g., McCoy et al., 1999), each evacuated silica tube (outer diameter 8mm; inner diameter 6 mm) was heated in the vertical furnace outside the alumina tube (Imae and Ikeda, 2008), with Ar gas flow (400 cc/min) into the tube (Table 1). The experimental charges were mounted in epoxy resin and dry polished. They were then observed using an optical microscope and a field emission scanning electron microscope with an energy dispersive spectroscopy (FE-SEM; JSM-7100F, JEOL, EDS; AZtecEnergy X-Max^N 50, Oxford), and phase composition was determined using an electron probe micro analyzer (EPMA; JXA-8200, JEOL).

Table 1. Experimental conditions and the summarized results.

Run#	Temperature (°C)	Duration (hr)*	Composition x of pyrhhotite nodule after heating, FexS	Fe# (at%) of Nng**
SCPo-7	1200	78.9	0.92	18-19
SCPo-8	1280	66	Not yet measured	15-16
EnPo-1	1200	44.7	0.89	11-13
EnPo-2	1280	72	0.92	13-14
DiPo-1	1200	44.7	0.92	-

*Isothermal heating period.

**Fe#=$x_{Fe}^{Nng}/(x_{Mg}^{Nng}+x_{Fe}^{Nng})$x100.

Results

The experimental products were summarized in Table 1. SCPo-7: Granular niningerite crystals were abundantly formed around olivines, which accompanied the silica phase (Fig. 2a). SCPo-8: Niningerite forms in the inner layer and silica in the outer layer (Fig. 2d). EnPo-1: The observation showed a similar result to the case of SCPo-1 (Fig. 2b). EnPo-2: Niningerite forms in the inner layer and silica in the outer layer (Fig. 2e). DiPo-1: Oldhamite crystals were formed around the diopside accompanying the silica phase and enstatite (Fig. 2c).

Discussion

Niningerite forms from the sulfidation of Mg-pyroxene as well as from that of Mg-olivine. However, it does not form from the diopside. Instead, oldhamite is formed from the diopside. Since enstatite is a major constituent phase in the EH3 chondrites, niningerite in EH3 chondrites would have originated from the sulfidation of enstatite, if we consider the sulfidation during the chondrule formation.

Fleet and MacRae (1987) showed experimentally that the sulfidation of magnesian olivine forms enstatite with niningerite. However, the present study (SCPo-7 and SCPo-8) did not produce enstatite but silica. The difference would be that Fleet and MacRae (1987) may have had a longer heating than the present study, as the longer heating may have formed enstatite by reaction of olivine and silica.

The Fe# of niningerite should be essential for estimating the precursor Mg-silicate compositions, although Fleet and MacRae (1987) did not report the Fe# of niningerite. Considering the partitioning of the Fe/Mg between starting material and product phases, the Fe# of niningerite may suggest that the precursor Mg-silicate is more ferroan than the Fe# in the clinoenstatite in the type BI chondrule in EH3 chondrites. However, this seems unlikely. During the annealing process, the reaction with the gaseous phase may result in the higher Fe# of niningerite, magnesium leaving niningerite, and manganese component entering niningerite.

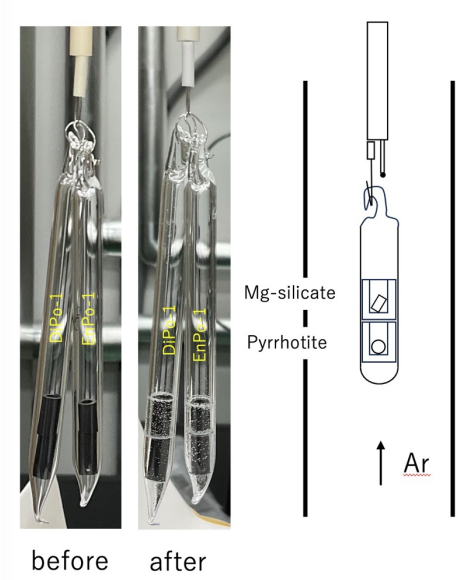

Fig. 1. Experimental assembly using an evacuated silica tube method. Mg-silicate and pyrrhotite are included in each graphite capsule. Left image: Before heating of DiPo-1 and EnPo-1. Right image: After heating. Mg-silicate = olivine, enstatite, or diopside. Please note that the silica tube was heated at 1200 ºC for several tens hours, but the silica was not devitrified since Ar gas flowed surrounding the tube during the heating and cooling. Mg-silicate corresponds to "chondrules", and pyrrhotite corresponds to "metal nodules" in enstatite chondrite. The higher pS_2 from pyrrhotite is produced in the tube than that from troilite and kamacite assemblage, resulting in the rapid sulfidation of silicates.

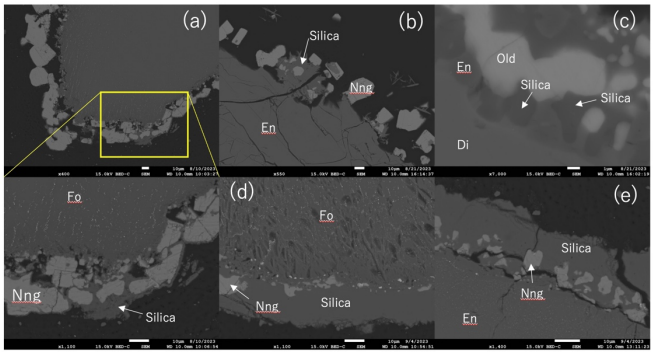

Fig. 2. Reaction products. Niningerite and silica formed by the sulfidation with forsterite and enstatite (a, b, d, e). Olhamite, silica, and enstatite formed by the sulfidation with diopside (c). They are granular euhedral shapes, ~10μm in grain size. The formed sulfides do not coherently contact with the substrate, but they occur with random orientation on the substrate. (a) SCPo-7. (b) EnPo-1. (c) DiPo-1. (d) SCPo-8. (e) EnPo-2. Fo=forsterite (San Carlos olivine, Fe#=8-9 at%). Nng=niningerite. En=enstatite (Fe#=8-9 at%). Di=diopside. Old=oldhamite.

Application to chondrule and metal nodule simultaneous formation

Silicate starting materials correspond to the components of chondrules and starting material pyrrhotite to the metal nodule. The reaction rate would be applied to the cooling system for the formation.

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