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Hydrothermal preparation of analogous matrix minerals of CM carbonaceous chondrites from metal alloy particles

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ABSTRACT

A mineral assemblage that is analogous to the matrix minerals of CM carbonaceous chondrites was produced from an alloyed metal particle mixture of Fe, Mg, Al, Si, and Ni in reducing, basic and S^2-containing hydrothermal environments. The elemental ratios of the alloyed metal particle mixture were adopted from reported matrix composition of the carbonaceous chondrite Murchison. The characteristic minerals of the synthetic mineral assemblage are cronstedtite, tochilinite and tochilinite–cronstedtite-intergrowth, other minerals include polyhedral serpentine, chrysotile-like phase, nanotube-like hollow structures, lizardite-like phase, brucite-like phase, etc. (not every mineral appears in a single sample, however, cronstedtite and tochilinite are two invariant minerals in the synthetic mineral assemblage). The dominant individual minerals in the synthetic mineral assemblage have remarkable similarity to the corresponding minerals of the matrix of CM carbonaceous chondrites in composition, morphology, structure, and crystallinity. Our experimental work indicates that matrix minerals of CM carbonaceous chondrites formed billions of years ago may be reproduced under laboratory conditions.

1. Introduction

The CM carbonaceous chondrites are chemically very primitive meteorites and are considered to have recorded much information about the evolution of the early solar system (Buseck and Hua, 1993). CM chondrites are composed of mixtures that include coarse-grained components such as Ca- and Al-rich inclusions (CAIs) and chondrules that are surrounded by fine-grained rims (FGRs) and fine-grained matrix materials. The matrix and FGRs of CM chondrites are mainly composed of low-temperature inorganic minerals such as various serpentines (mainly cronstedtite and other Mg-rich and Fe-bearing serpentine group minerals), tochilinite, tochilinite–cronstedtite-intergrowth (TCI, which has ever been named as TSI (tochilinite–serpentine-intergrowth) in the authors' previous work Peng et al., 2007), carbonates, pyrrhotite, pentlandite, etc. (Buseck and Hua, 1993; Zolensky et al., 1993).

The matrix and FGRs minerals of CM chondrites are generally considered to be the products of hydrothermal alteration of high-temperature phases such as olivine (with varying Fe contents), pyroxene, igneous glass, amorphous silicates, CAIs (Buseck and Hua, 1993). Hence, there are a number of simulated hydrothermal experiments during the past 20 yr that are designed to reproduce the matrix minerals in laboratory (e.g., Takatori et al., 1993; Nomura and Miyamoto, 1998; Iishi and Han, 2000; Ohnishi, 2003; Jones and Brearley, 2006; Ohnishi and Tomeoka, 2007; Noguchi et al., 2011). A typical characteristic of these simulated hydrothermal experiments is that they are generally carried out in relatively oxidizing environments and always produced Mg-rich phyllosilicates (e.g. Mg-rich serpentine and saponite) and amorphous and/or crystalline Fe oxides or hydroxides (e.g. FeO (OH), Fe_3O_4). However, the important Fe-rich minerals like cronstedtite, tochilinite and TCI of CM carbonaceous chondrites have not been reported to be reproduced this way.

Contrary to the above simulated hydrothermal experiments, the successful syntheses of tochilinite and TCI have been carried out in strictly O_2-free and reducing environment (Kakos et al., 1994; Kozerenko et al., 1996, 2001; Peng et al., 2007, 2009). Theoretical study on tochilinite indicated that tochilinite must be prepared in a reducing environment (log(oxygen fugacity) or $\log(f_{O_2(g)}) < -85$ or $Eh < -0.45$ V at standard temperature and pressure (STP, 25 °C and 10^5 Pa); Zolensky, 1984; Browning and Bourcier, 1996). Early studies on the low-temperature synthesis of Fe-rich phyllosilicates (trioctahedral ferrous or dioctahedral ferric) have shown that they must be prepared (at least initially) in a reducing environment

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(Eh ≤ -0.6 V; Harder, 1978, 1980), though the obtained products usually have a low crystallinity.

Most recent synthetic experiments have shown that cronstedtite can be prepared from Fe metal and smectite (or smectite + quartz) in a hydrothermal environment that is O_2-free, basic, reducing and aqueous silicon oxide-bearing (Lanson et al., 2012; Pignatelli et al., 2013). Because Fe metal in anoxic and neutral to basic aqueous solution first corrodes to form $Fe(OH)_2$ (Odziemkowski et al., 1998; Reardon, 2005), the synthesized cronstedtite can be considered as being prepared from $Fe(OH)_2$. As iron and magnetite are always associated together with the product cronstedtite in such reaction system, the oxygen fugacity can be considered not far from the Fe-magnetite buffer (i.e. $\log(f_{O_{2(g)}}) \approx -89$ at STP or Eh < -0.50 V).

Then, why these Fe-rich minerals cannot form in an oxidizing environment? A typical feature of these minerals like tochilinite, TCI and cronstedtite, is that they all contain $Fe(OH)_2$ or $Fe(OH)_2$-like layers (e.g. in the structure of cronstedtite) (Organova et al., 1974; Mackinnon and Zolensky, 1984; Peng et al., 2009; Pignatelli et al., 2013). Of course, the octahedrally coordinated iron in such layers can be replaced by other cations such as Mg^{2+}, Fe^{3+} and Al^{3+}. Considering the viewpoint of Harder (1978, 1980), the successful synthesis of Fe-rich phyllosilicates appears to be determined by the stability of $Fe(OH)_2$ under the synthetic conditions. If the synthetic condition can assure the stability of $Fe(OH)_2$, then Fe-rich phyllosilicates can form. However, if the synthetic condition cannot assure the stability of $Fe(OH)_2$, Fe-rich phyllosilicates have no chance to form. This viewpoint can be extended to the synthesis of other Fe-rich layered minerals containing $Fe(OH)_2$ or $Fe(OH)_2$-like layers, like tochilinite and TCI. Thus, the difficulty of the synthesis of the Fe-rich minerals can be simplified as how to keep the stability of $Fe(OH)_2$ under specific reaction conditions. However, only ultra-pure $Fe(OH)_2$ is a relatively stable material below 100 °C under strictly O_2-free condition, $Fe(OH)_2$ co-existed with some "catalytic" materials or impurities (e.g. Ni^{2+} ions, nickel hydroxide, nickel metal) is very unstable even under strictly O_2-free environment, and the time of its stability is from minutes to hours or days (Schikorr, 1929; Evans and Wanklyn, 1948; Shipko and Douglas, 1956; Schrauzer and Guth, 1976). $Fe(OH)_2$ is sparingly soluble in neutral to basic aqueous solution (Leussing and Kolthoff, 1953), and in anaerobic environment it mainly decomposes into magnetite (Fe_3O_4), H_2 and H_2O ($3Fe(OH)_{2(s)} = Fe_3O_{4(s)} + H_{2(g)} + 2H_2O_{(l)}$; $\Delta G^{\theta}_{R} = -RT \ln K = -27.35$ kJ/mol; $K = P_{H_2} = 6166$ MPa; Reardon, 2005). The generation of magnetite and H_2 has been used to calibrate the decomposition process of $Fe(OH)_2$. But, it has been found that aqueous silicon oxide can stabilize such unstable $Fe(OH)_2$, and such a stabilizing effect is suggested to involve the formation of (probably layered) ferrous silicate (Shipko and Douglas, 1956). The successful preparation of cronstedtite from Fe metal (or, say directly, from $Fe(OH)_2$) and smectite (or smectite + quartz) in O_2-free, basic, reducing and aqueous silicon oxide-bearing environment confirmed the stabilizing ability of aqueous silicon oxide (Odziemkowski et al., 1998; Reardon, 2005; Lanson et al., 2012; Pignatelli et al., 2013), thus, indirectly proved that Harder's viewpoint about the synthesis of Fe-rich phyllosilicates is correct. However, the reaction conditions are not perfect as a lot of magnetite was found to co-exist with the synthesized cronstedtite, which suggests that considerable amount of the intermediate $Fe(OH)_2$ decomposed into magnetite and was not used to form cronstedtite.

In addition, the successful preparation of tochilinite and TCI may, to some extent, also show that Harder's viewpoint is correct, but the structures of tochilinite and TCI indicate that the $Fe(OH)_2$ or $Fe(OH)_2$-like layers can also be stabilized by mackinawite-like $Fe_{1-x}S$ layers in aqueous solution (Kakos et al., 1994; Kozerenko et al., 1996, 2001; Peng et al., 2007, 2009).

Then, the direct synthesis of the Fe-rich matrix minerals (e.g. Fe-rich phyllosilicates, TCI and tochilinite) of CM carbonaceous chondrites demands that proper amount of $Fe(OH)_2$, aqueous silicon oxide, S^{2-} ions must exist in a basic and reducing hydrothermal solution simultaneously (of course, other components are also needed, e.g. Mg^{2+} and Al^{3+} ions and/or their hydroxides). The reaction conditions (e.g. temperature, pressure and $f_{O_{2(g)}}$) must assure that $Fe(OH)_2$ is stable until enough aqueous silicon oxide can combine with it, otherwise would result in a lot of magnetite to be produced, while magnetite is a minor matrix mineral of CM chondrites (Buseck and Hua, 1993; Zolensky et al., 1993). From the standpoint of synthetic chemistry, we think that the easy choice to synthesize the matrix minerals of CM carbonaceous chondrites is employing pure metals or their alloys to perform the synthesis, as the dissolution rates of different metals are not extremely large. It is not easy to produce such an environment by the hydrothermal treatment of extant chondritic high-temperature minerals (i.e. olivine (with varying Fe contents), pyroxene, igneous glass, amorphous silicates, CAIs) alone or the mixture of these high-temperature minerals and Fe metal, as the dissolution rates of these high-temperature minerals, are fairly slower compared with the dissolution rates (or corrosion rates) of metals (e.g. metallic Fe) (e.g. Hänchen et al., 2006; Reardon, 2005; Peng et al., 2009; Gudbrandsson et al., 2011).

In our previous work (Peng et al., 2007), we reported that FeMgAl tochilinite and TCI can be hydrothermally prepared from a partially alloyed metal particle mixtures of Fe, Mg, Al, Si, Cr, and Ni in basic and reducing environments. In the present work, we push our research forward by synthesizing the dominant minerals of the matrix of CM carbonaceous chondrites from alloyed metal particle mixtures of Fe, Mg, Al, Si, and Ni, with elemental ratios adopted from reported matrix composition of the CM chondrite Murchison (McSween, 1987), in reducing, basic and S^{2-}-containing environments. The applications of our experimental results to meteoritics are discussed.

2. Materials and methods

All the metal powders were purchased from Shanghai Chemical Reagents Company, and the purity and sizes of them are listed in Table A1 in the Appendix. The alloyed metal particle precursor mixture (MPPM) was prepared in a way similar to our previous method (Peng et al., 2007). For one preparation run, 25.95 g Fe (0.46 mol), 10.41 g Si (0.37 mol), 8.44 g Mg (0.35 mol), 1.46 g Al (0.05 mol), and 1.61 g Ni (0.03 mol) were used. The elemental ratios of the MPPM are derived from the matrix composition of the CM chondrite Murchison (McSween, 1987), supposing that the reported elemental ratios indeed reflect the chemical composition of the matrix of the chondrite Murchison. The metal powders were first mixed visually homogeneous and pressed into pellets. The pellets were then heated in a tube furnace in an Argon atmosphere at 950–980 °C for 3 h. After cooling to room temperature (within 2–3 h), the pellets were ground into micrometer-sized powder in air in a short time and then used for the hydrothermal synthesis. X-ray powder diffraction (XRD) analysis of the MPPM (Fig. A1 in the Appendix) showed that alloying of the raw metal powders has occurred.

The hydrothermal reaction was carried out in the temperature range of 106–160 °C for short-duration runs (initial exploratory experiments), but for long-duration runs, the reaction temperature was fixed at 153 °C. These temperatures are generally comparable with the alteration temperatures of carbonaceous chondrites deduced from the characterization of the minerals of the matrix and FGRs of them (Zolensky et al., 1993). In a typical preparation run, 0.69–4.3 g MPPM, 1.9–77.1 mmol of $Na_2S \bullet 9H_2O$ and 35–48 mL of distilled water were sealed into a Teflon-lined stainless steel