

## Research Article

# A Metastable Aluminosilica Compound for Aluminum and Water Transport to the Upper Mantle

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It has been suggested that crystalline “phase egg,”  $\text{AlSiO}_3\text{OH}$ , with a ratio  $\text{Al/Si} = 1$  could carry aluminum and water to the mantle but its natural occurrences are still speculative. An amorphous phase with a fixed and unique, deep metastable eutectic  $\text{Al}_2\text{Si}_2\text{O}_7$  composition was produced in laboratory experiments wherein conditions favored kinetically controlled formation of amorphous solids. This experimentally produced kaolinite-dehydroxylate is highly reactive and it is proposed as the precursor of phase egg in subducting slabs of crustal rocks. If so, metastable phases play a role in subduction zones and it then follows that the processes and resulting conditions in these environments can be nonuniform and discontinuous at least at micrometer scales.

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## 1. Introduction

The presence of aluminous phases in the upper part of the mantle is still a matter of debate that stands apart from the question of whether such phases are thermodynamically stable or not. It is unlikely that such aluminous phase will exist in the lower mantle at 70–135 GPa, that is, between ~1500 and 2900 km [1]. Aluminous phases were considered as potential carriers of aluminum and water (OH) to the mantle in subduction zones with aluminum hosted in a high-pressure form of  $\text{Al}_2\text{SiO}_5$  [2]. Other experiments concluded that there could be no aluminous phase in the mantle, only Mg- and Ca-perovskite and magnesiowüstite [3]. Water could be carried in subducting slabs by OH-bearing minerals such as topaz-OH or “phase egg” [4]. The latter hydrated aluminum silicate potentially forms in rocks of wide-ranging bulk compositions [4], and could be a significant carrier of aluminum and water. Still, natural occurrences of phase egg are speculative [4] although laboratory experiments simulating the subduction of sediments showed that “phase egg” is stable between 1100 and 1300°C at 15 GPa [5]. Phase egg,  $\text{Al}_5\text{Si}_5\text{O}_{17}(\text{OH})$ , was named after

R. E. Eggleton. Crystalline phase egg was synthesized from  $\text{H}_2\text{O}$ -bearing aluminosilica gels, kaolinite, or pyrophyllite above 1000°C at >10 GPa [6]. These experiments did not reach complete equilibrium but established a unique phase egg  $\text{Al/Si} = 1$  atomic ratio that only formed when the starting materials contained substantial amounts of water. Other synthesis experiments at >11 GPa and 700°C on mixtures of cristobalite,  $\text{Al}_2\text{O}_3$ , and  $\text{Al}(\text{OH})$  refined the “phase egg” crystal structure with an ideal structural formula  $\text{AlSiO}_3\text{OH}$  with 7.5 wt% stoichiometric water [7]. However, the strong hydrogen bonding and Al-Si disorder that support high pressure and high temperature stability of phase egg [8] are unrelated to its thermodynamic stability or metastable nature. Phase egg is a metastable mineral stabilized by incorporating OH at high pressures.

Albeit under much different, highly kinetic conditions an amorphous material with a “peculiar  $\text{Al/Si}$  ratio close to 1” was found in the Haughton impact crater (Canada) that experienced peak impact pressures between 50 and 60 GPa and temperatures of 1400 to 2500°C followed by thermal decay to ~1200°C in a few milliseconds [9]. This example shows that an anhydrous metastable, amorphous,

TABLE 1: Composition (oxide wt%) of phase egg (calculated on a water-free basis) obtained in laboratory simulation experiments [7, 8], including a sediment analog that contained minor <1.5 wt%, TiO<sub>2</sub>, FeO, trace amounts (<0.52 wt%) of MgO, CaO, Na<sub>2</sub>O, and K<sub>2</sub>O, and 6 wt% H<sub>2</sub>O [5], and the vapor-condensed, amorphous, metastable eutectic aluminosilica compound [10].

Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Source
Phase egg		
44.9	55.1	[7]
45.5	54.5	[7]
45.6	54.1	[7]
45.9	54.1	[8]
Subducting sediment experiment		
44.2	55.8	[5]
Metastable aluminosilica compound		
46.7	53.3	[10]

or crystalline, aluminosilica solid with Al/Si = 1 can exist in nature due to kinetically controlled processes.

In this paper we present an amorphous, metastable aluminosilica compound with the unique Al/Si ratio of phase egg (Table 1) that does in fact arise systematically under nonequilibrium conditions that, in our case, were simulated by condensation of Al-SiO-H<sub>2</sub>-O<sub>2</sub> vapors [10, 11]. Once formed, its metastable nature will readily facilitate hydration to “phase egg.”

## 2. Laboratory Experiments and Sample Analyses

Gram quantities of porous aggregate samples, called smokes were produced in Condensation Flow Apparatus that was specifically designed to capture condensation process in its earliest stages of solid condensate formation. Details of this apparatus and the experimental conditions to produce the condensate samples are provided in [12, 13]. Grain formation is a stochastic process that occurred far from chemical equilibrium. The condensed aggregates often consist of hundreds or even thousands of individual amorphous grains of two mixed metal-oxide compositions, namely, aluminosilica (AlSiO) grains. Each grain is connected to only two or three neighboring grains. The condensate grain sizes range from ~2 nm up to ~100 nm in diameter. Individual grains in the ultra-thin sections (~70 nm) of the samples were characterized using a JEOL 2000FX Analytical Transmission Electron Microscope (ATEM) that was operated at an accelerating voltage of 200 keV and was equipped with a Tracor-Northern TN-5500 energy-dispersive spectrometer (EDS) for in situ analyses. The standard Cliff-Lorimer thin film procedure was for EDS data reduction [14] using calibrated *k*-factors. Details of the otherwise standard ATEM procedures are provided in [9, 10]. Standard selected area electron diffraction was used to determine the crystallographic properties, that is, crystalline (mineral) or amorphous. The typically diffuse ring patterns

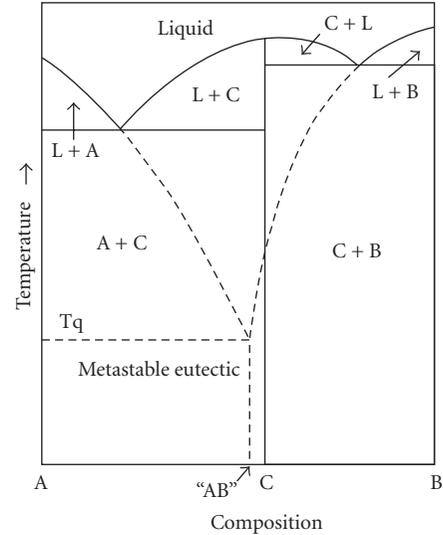


FIGURE 1: The hypothetical binary equilibrium phase diagram A-B showing the position of a (deep) metastable eutectic with a composition “AB” defined at the intersect of the metastable extensions of the liquidus surface (dashed lines) and located in between the compositions of both (stable) eutectic points on the liquidus surface at the top of the diagram (solid lines). This figure was modified after [18].

without diffraction maxima indicated that these condensed aluminosilica grains were amorphous solids.

## 3. Amorphous Aluminosilica Compounds

The aluminosilica grains between ~2 nm and ~25 nm that formed during condensation of Al-SiO-H<sub>2</sub>-O<sub>2</sub> and Fe-Al-SiO-H<sub>2</sub>-O<sub>2</sub> vapors had compositions that do not match any stoichiometric mineral composition. The mean Al<sub>2</sub>O<sub>3</sub> (wt%) contents of these amorphous grains present two Gaussian distributions, namely, (1) 11.5 ± 3 (range: 6–16) and (2) 46.7 ± 10.8 (range: 22–71) [10]. The second aluminosilica composition is between the two eutectic compositions in the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram at ~10 wt% Al<sub>2</sub>O<sub>3</sub> and ~80 wt% Al<sub>2</sub>O<sub>3</sub> [15]. It is a common and reproducible feature in the nonequilibrium vapor phase condensation experiments [12, 13, 16, 17].

The unique deep metastable eutectic (DME) compositions are constrained by the presence of stable eutectics (Figure 1). This hypothetical phase diagram A-B has two eutectics. When the equilibrium phase boundaries (solid lines) are extended towards lower temperatures (dashed lines) they will intersect at the intermediate composition “AB.” AB is the composition of a DME compound. Its composition is the mean of the measured smallest grain compositions. The quench temperature (T<sub>q</sub>) of the condensation experiment is used to plot its position in the diagram, which is typically well below the glass transition temperature. Being a metastable feature it cannot have a fixed temperature in an equilibrium phase diagram. Its composition is the main feature of invariably amorphous DME compounds.

The compositions of DME solids are insensitive to the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the condensing vapor.

The mean composition,  $46.7 \pm 10.8$  wt%  $\text{Al}_2\text{O}_3$  (Table 1), identifies this phase as a DME kaolinite-dehydroxylate ( $\text{Al}_2\text{Si}_2\text{O}_7$ ). This unique aluminosilica composition coincides with the crest of the metastable immiscibility gap and spinodal in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  phase diagram [19]. They separate silica-rich, glass forming from alumina-rich, poor glass-forming compositions [20]. This particular thermodynamic configuration presents ample opportunities to yield a metastable  $\text{Al}_2\text{Si}_2\text{O}_7$  compound that can be precursor for metastable “phase egg.”

The condensed DME dehydroxylate grains formed during chaotic cycles when the vapor condensation rates exceeded condensate evaporation rates prior to equilibrium condensation when the gas and grains temperatures had equalized [21]. The solids surviving from the pre-equilibrium regime are dissipative structures that are defined [22] as states of organization of matter where disequilibrium has become a source of order. The prerequisite conditions to form such dissipative structures are (1) supercooling into the solid phase field from high-temperatures in the vapor or liquid phase fields, and (2) at least two stable eutectic points in the phase diagram. When, as many Earth Scientists believe, metastable phases cannot play any role as a natural mineral of the mantle or of subduction zones [23] the key word is “mineral.” There is no a priori and obvious reason that metastable compounds could not exist in these environments as a result of kinetic inhibition. An example of natural metastable equilibrium would be sillimanite in aluminosilicate mineral assemblages in high-grade to ultrahigh-grade, aluminous metamorphic rocks [24]. It is too soon to dismiss the possibility of metastable equilibrium and thus the presence of naturally occurring “metastable minerals” and compounds.

#### 4. Discussion

The deep metastable eutectic kaolinite dehydroxylate,  $\text{Al}_2\text{Si}_2\text{O}_7$ , is an amorphous compound with a unique Al/Si ratio of unity. Like this anhydrous dehydroxylate, a “phase egg” precursor will be insensitive to the bulk composition of its environment. Metastable “phase egg” would form by high-pressure stabilization [8] during hydration of the amorphous  $\text{Al}_2\text{Si}_2\text{O}_7$  compound in a reaction



Water for this reaction is probably not a limiting factor in subducting slabs of continental rocks.

We do not know the nature or the extent of small-scale physicochemical processes that may exist in a descending slab or their continuity. At temperatures  $>1000^\circ\text{C}$ , we can only guess what conditions could cause the rapid supercooling required to form the highly metastable kaolinite dehydroxylate compound. Perhaps earthquakes are a triggering mechanism to create small-scale conditions of supercooling. The other question is how the necessary chemical conditions for a metastable phase egg precursor could be achieved.

We suggest two potential pathways, namely, (1) petrological phase changes due to changing pressures and temperatures in subducting sediments [5] and (2) decomposition of cordierite that is being carried downward [25]. In this context, it is noteworthy that laboratory experiments to determine cordierite stability were plagued by metastable equilibrium [26–28] and its thermodynamic stability is still not fully resolved. An amorphous metastable  $\text{Al}_2\text{Si}_2\text{O}_7$  compound that is the phase egg precursor could form by decomposition of metastable cordierite in a reaction



As the water content of cordierite decreases with depth and pressure [29], water required in (1) was freed during this reaction (2).

#### 5. Conclusions

Natural occurrences of phase egg to transport water and aluminum to the mantle are speculative and its role is uncertain. Equally uncertain is the notion that metastable minerals and compounds could exist in subducting slabs. Phase egg’s atomic ratio Al/Si = 1 is unique. Accepting that a kaolinite phyllosilicate could not exist in descending slabs, the experimentally verified existence of an amorphous, deep metastable eutectic, kaolinite-dehydroxylate compound offers a possibility that phase egg might exist naturally as a metastable mineral. Once formed in the slabs of crustal rocks, this  $\text{Al}_2\text{Si}_2\text{O}_7$  compound becomes a precursor of a natural metastable “phase egg” mineral,  $\text{AlSiO}_3\text{OH}$ . A major unknown at this time is whether transient microenvironments can be created in these slabs that provide the requisite thermodynamic conditions to form the  $\text{Al}_2\text{Si}_2\text{O}_7$  aluminosilica precursor.

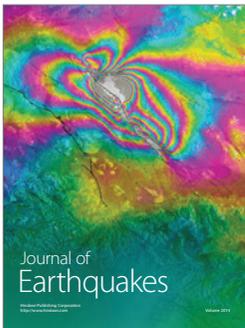
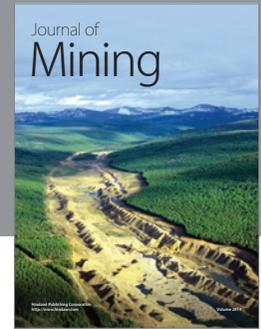
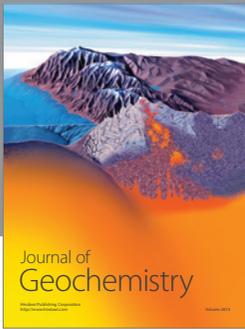
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