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Biogeochemical silicon cycle and carbon sequestration in agricultural ecosystems

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ABSTRACT

Global agricultural ecosystems, the largest biospheric sources of atmospheric carbon dioxide (CO_2), may turn into considerable net carbon (C) sinks through adopting management strategies advised by research. As C sequestration is usually coupled with the silicon (Si) cycle, strategic manipulation of the biogeochemical Si cycle in agricultural ecosystems offers a not yet fully explored possibility to enhance C sequestration. This review summarizes current knowledge of C sequestration coupled with the Si cycle and its management in agricultural ecosystems. Carbon sequestration is coupled with the Si cycle through many processes including dynamics of phytoliths and aggregates, and silicate weathering at different temporal and spatial scales. Cultivation of deep rooting crops, erosion mitigation with buffer strips, fertilization of Si-rich materials are some of the potential management strategies to increase both crop production and C sequestration coupled with the Si cycle. Further questions such as identifying the controlling factors of bioavailable Si pools and C sequestration, and quantifying the cost-efficiency of different management strategies to manipulate the Si cycle with the aim to enhance C sequestration should be investigated.

Contents

1. Introduction

Agricultural ecosystems cover a global area of 15.33×10^8 ha and play a key role in the terrestrial carbon (C) balance (Lal, 2004a,b; Piao et al., 2009; Song et al., 2013a). Although global agricultural ecosystems are the largest biospheric sources of atmospheric CO_2 (Houghton et al., 1999; Smith, 2004), they may turn into considerable net C sinks under strategic management (Lal, 2004a,b; Six et al., 2004; Piao et al., 2009; Song et al., 2013a, 2014; Six and Paustian, 2014).

Silicon (Si), an abundant element of the land surface, is of great concern to ecologists, biogeochemists and agronomists. It is coupled with C in many biogeochemical processes including diatom C pump, dynamics of phytoliths and aggregates, and silicate weathering, and thus may regulate long-term atmospheric CO_2 concentration and climate change (Street-Perrott and Barker, 2008; Li et al., 2011; Song et al., 2012a; Struyf and Conley, 2012). Silicon also contributes to crop resistance to biotic (e.g., pathogens and pests) and abiotic (e.g., nutrient imbalances, heavy metal toxicity, salinity and water stress) stresses (Epstein, 1994; Guntzer et al., 2012a; Vandevenne et al., 2012; Zhu and Gong, 2014).

Silicon is particularly prolific (>10 mg Si g^{-1} of dry weight) in many crops including rice (*Oryza sativa*) (Li et al., 2013), wheat (*Triticum* sp.) (Parr and Sullivan, 2011; Gocke et al., 2013), maize (*Zea mays*) (Song et al., 2014), millet (*Panicum miliaceum*) (Zuo and Lü, 2011) and sugarcane (*Saccharum officinarum*) (Parr et al., 2009). Global cultivation and harvest of crops may export 50–100 kg Si ha^{-1} $year^{-1}$ (Meunier et al., 2008) or 220–820 Tg Si yr^{-1} (1 Tg $= 10^{12}$ g, Matichenkov and Bocharnikova, 2001; Carey and Fulweiler, 2012), while the net river export of Si to the oceans has been estimated as 140 Tg Si yr^{-1} (Tréguer et al., 1995). The agricultural export of Si from crop cultivation and harvest may deplete soils' labile Si pools (Meunier et al., 2008; Clymans et al., 2011; Keller et al., 2012; Vandevenne et al., 2012; Barão et al., 2014). Si management in agricultural ecosystems thus offers a possibility to enhance both crop production and C sequestration (Song et al., 2012a).

Despite the importance of Si for multiple crops and the large contribution of agricultural ecosystems to the global C balance, mechanisms and management of Si–C interactions in agricultural ecosystems have not been well documented (Li et al., 2011; Song et al., 2012a). This is the topic of this review. We first introduced biogeochemical Si cycle in agricultural ecosystems. Then, we briefly reviewed three mechanisms of C sequestration coupled with silicon cycle: (1) phytolith C sequestration, (2) organic C stabilization in agricultural soils, and (3) CO_2 consumption from silicate weathering. At the end of these sections, we discussed feedbacks of C sequestration processes under different topographic conditions.

2. Biogeochemical Si cycle in agricultural ecosystems

Cereals and many other cultivated crops are Si accumulators (Datnoff et al., 2001; Ma and Takahashi, 2002; Hodson et al., 2005). In contrast to less managed terrestrial ecosystems, a significant proportion of the Si accumulated in cultivated crops is harvested and does not directly return to the soil (Desplanques et al., 2006; Clymans et al., 2011; Vandevenne et al., 2012; Barão et al., 2014). For agricultural ecosystems, the main Si sources include atmospheric, groundwater, irrigation and fertilization inputs, while the main Si exports include crop harvest, leaching and erosion losses (Desplanques et al., 2006; Clymans et al., 2011; Vandevenne et al., 2012; Barão et al., 2014). The

biogeochemical Si cycle in agricultural ecosystems consists of multiple processes and Si pools (Fig. 1).

2.1. Crop Si uptake and phytolith formation

Crops take up Si mainly in the form of monomeric silicic acid [Si(OH)$_4$ or H_4SiO_4] from soil solutions (Mitani et al., 2005; Ma et al., 2006). Silicon accumulation varies significantly among crop species (Hodson et al., 2005; Liang et al., 2006; Mitani et al., 2009; Cooke and Leishman, 2011) as the density of transporter (e.g., SIT1) differs with crop species (i.e. rice > cucumber > tomato) (Mitani and Ma, 2005; Mitani et al., 2005; Ma and Yamaji, 2006). Silicon is concentrated and polymerized to form silica gel in the shoot of crops owing to transpiration (Ma and Yamaji, 2006). Silica gel is finally deposited as phytoliths in the cell wall, intercellular space, and cell luminas (Ma and Yamaji, 2006). The detailed description of plant Si uptake process can be found in recent reviews such as Cooke and Leishman (2011).

Phytoliths contain about 90% of silica, 1 to 6% of organic carbon, and trace amounts of other components such as aluminum and iron (Bartoli and Wilding, 1980; Bartoli, 1985; Alexandre et al., 1997; Parr and Sullivan, 2005, 2011). About 90% of silica in plants is hosted in phytoliths, thus a plant's phytolith content can be estimated from a plant's silica content (Wang, 1998; Song et al., 2013a, 2014). Phytolith content in crops varies with tissue (Li et al., 2013), age (Ma and Yamaji, 2006), species (Perry et al., 2006; Parr and Sullivan, 2005, 2011; Li et al., 2013) and cultivars (Parr and Sullivan, 2011). Within the same plant, the contents of phytoliths in crop sheath and leaf are much higher than those of grain and stem (Li et al., 2013). More phytoliths accumulate in older tissues than in younger tissues because Si is no longer mobile once it has been polymerized and deposited within plants (Ma and Yamaji, 2006). Rice, wheat, maize, and sugarcane accumulate much more phytoliths (>30 mg g^{-1} phytoliths) than other crops (<10 mg g^{-1}) (Hodson et al., 2005; Perry et al., 2006; Parr et al., 2009; Parr and Sullivan, 2011). Among different wheat (*Triticum* sp.) cultivars, phytolith content also varies from 26.8 mg g^{-1} to 78.5 mg g^{-1} (Parr and Sullivan, 2011).

Rice, maize and wheat are the main crops contributing to the global crop phytolith production because of their large distribution areas and high phytolith production fluxes with 617 ± 132 kg ha^{-1} $year^{-1}$, 404 ± 116 kg ha^{-1} $year^{-1}$ and 342 ± 114 kg ha^{-1} $year^{-1}$, respectively (Carey and Fulweiler, 2012; Rajendiran et al., 2012; Song et al., 2014). The global crop phytolith production rate was estimated by Carey and Fulweiler (2012) to be 29.41 Tmol Si yr^{-1} (1764 Tg SiO_2 $year^{-1}$). This value is much higher than the estimates by Rajendiran et al. (2012) (167 to 286 Tg SiO_2 $year^{-1}$) and Song et al. (2013a) (240 ± 66 Tg SiO_2 $year^{-1}$), and these differences can be explained by the use of different data sources.

2.2. Harvest and return of Si

In less managed terrestrial ecosystems, most plant phytoliths are returned to soil either through plant litter fall or root decomposition (Bartoli, 1983; Alexandre et al., 1997). In contrast, a substantial proportion of phytolith produced in crops is taken from the site during harvest (Meunier et al., 2008).

After crop harvest, some phytolith-Si in crop straw and/or roots may be returned directly (Wickramasinghe and Rowell, 2006; Seyfferth et al., 2013; Ngoc Nguyen et al., 2014) or indirectly as biochar-Si (Houben et al., 2014; Liu et al., 2014) to the site. Some harvested Si will be transformed to human and animal waste Si after food/fodder
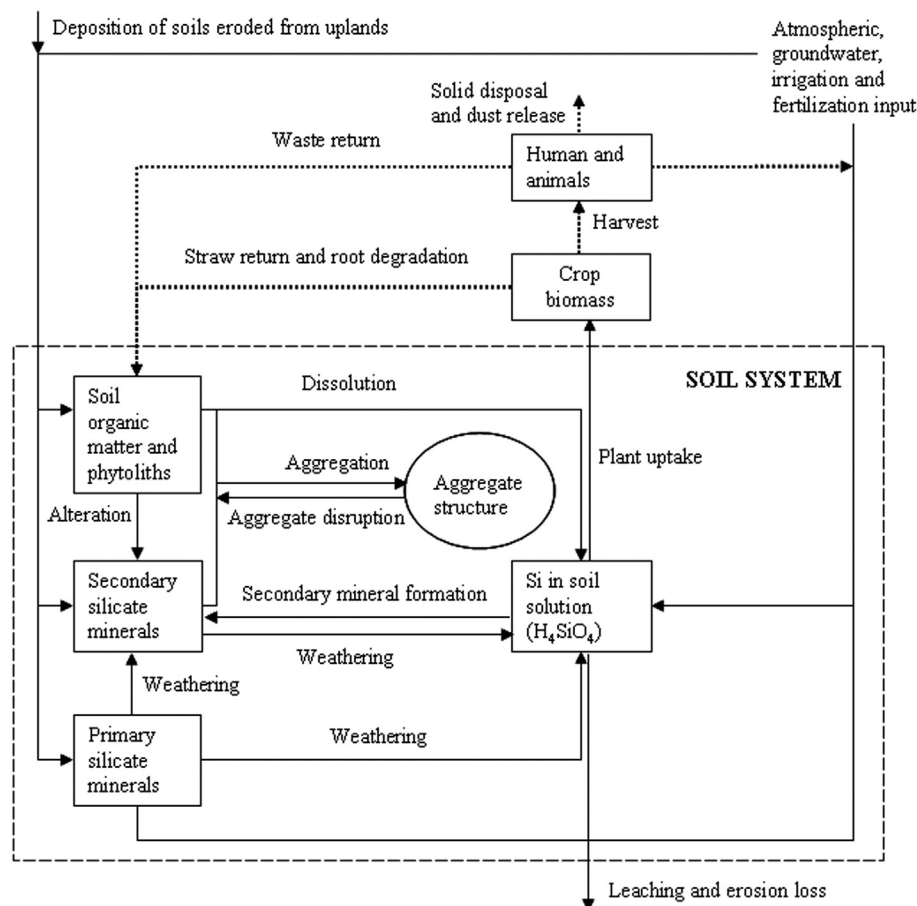
Fig. 1. Conceptual model of the biogeochemical Si cycle in agricultural ecosystems. Solid lines and arrows represent natural processes. Dotted lines and arrows represent processes that are mainly depending on human activities. The dashed line box represents the soil system.

consumption, and either returned to the soils as waste amendment or discharged into sewage plant systems and surface water bodies (Sferratore et al., 2006; Song et al., 2011; Vandevenne et al. 2012; Song et al., 2013b).

2.3. Dissolution and accumulation of soil phytoliths

After the decomposition of returned straws and/or roots, phytoliths are released into soils (Wickramasinghe and Rowell, 2006; Seyfferth et al., 2013) and may accumulate if their return flux is higher than their fluxes of erosion and dissolution (Cornelis et al., 2011a,b; Song et al., 2012a). Based on Si sorption isotherms and concentration changes in soil suspension experiments, Wickramasinghe and Rowell (2006) estimated that 10 to 20% of the phytoliths from rice straw can be dissolved depending on the soil composition of Si, Fe and Al. However, a decrease in soil pH may reduce the phytolith dissolution rate (Fraysse et al., 2009; Keller et al., 2012).

The return flux of phytolith may affect the distribution pattern and stock of phytoliths in soils (Parr and Sullivan, 2005; Keller et al., 2012). Clymans et al. (2011) found that the distribution of phytoliths in agricultural soils tended to have maximal phytolith concentrations in the topsoils. In contrast, under similar climatic conditions, Guntzer et al. (2012b) found that the phytolith concentrations in agricultural soils under cultivation increased with depth mainly due to continuous removal of wheat straw from the soils. Soil's phytolith stocks in mixed cereal land and pasture (13.5 and 12.8 t Si ha^{-1}, respectively) were much larger than the stock in soils under long-term wheat cultivation (6.5 t Si ha^{-1}) partly due to the higher phytolith return flux of the crop rotation in comparison to wheat (Clymans et al., 2011; Guntzer et al., 2012b; Keller et al., 2012). However, the stock and accumulation

of phytoliths in soils are not only dependent on the return rate of crop phytoliths but also on the geochemical stability of phytoliths (Song et al., 2012a).

Besides environmental conditions, the morphology and chemical composition of phytoliths influence the geochemical stability of phytoliths (Bartoli and Wilding, 1980; Bartoli, 1985; Alexandre et al., 1997; Blecker et al., 2006; Wickramasinghe and Rowell, 2006). Generally, granular (spherical or quasi-spherical) phytoliths in a crop's straw have a lower exposure degree and are more difficult to dissolve than other phytoliths (Kaufman et al., 1985; Balasta et al., 1989; Ma and Takahashi, 1989; Wickramasinghe and Rowell, 2006). Phytoliths containing more organic carbon are more stable than those containing less organic carbon (Clarke, 2003). Phytoliths with lower content of water and ratios of Si/Al and Si/Fe usually have lower solubility (Bartoli and Wilding, 1980; Bartoli, 1985; Wickramasinghe and Rowell, 2006).

2.4. Alterations in soil Si pool size and speciation

Although Si may be exported from agricultural ecosystems through crop harvest, leaching and erosion losses, some natural processes including silicate weathering, atmospheric deposition and deposition of soils eroded from uplands may refresh Si in agricultural ecosystems (Fig. 1). If Si was removed at the same rate as it was produced, agricultural ecosystems would be in a Si dynamic equilibrium. But continuous crop cultivation and harvest with little straw return or Si fertilization to the croplands may lead to depletion of a soil's Si pools (Meunier et al., 2008; Clymans et al., 2011). Soil erosion rates of agricultural ecosystems are usually higher than soil production rates causing net loss of Si from agricultural ecosystems (Montgomery, 2007; Quinton et al., 2010). It

has been reported that a depletion of Si from crop harvesting is usually coupled with a decrease in soil pH and yield (Savant et al., 1997a,b; Meunier et al., 2008; Keller et al., 2012; Vandevenne et al., 2012).

The Si pools in cropland soils can be divided into dissolved Si (DSi), adsorbed Si, biogenic Si (BSi), litho-/pedogenic amorphous silica (LSi) and crystalline Si according to their status and origin (Dietzel, 2000; Matichenkov and Bocharnikova, 2001; Sommer et al., 2006; Cornelis et al., 2011b). The dominant form of DSi in cropping soils under most conditions (pH < 9) is monomeric silicic acid [$Si(OH)_4$ or H_4SiO_4] (Matichenkov and Bocharnikova, 2001; Seyfferth et al., 2013). The concentration of Si in the soil solution of cropland soils ranges from 0.1 to 0.6 mM for most pH conditions (pH 1–9) depending not only on the solubility of the soils' primary and secondary Si compounds but also on Si removal through crop harvest, and Si inputs through, for example, irrigation and fertilization (Ma et al., 2006; Wickramasinghe and Rowell, 2006; Gocke et al., 2013; Seyfferth et al., 2013).

DSi is the direct source of Si to all crops, while adsorbed Si, BSi, LSi, and some crystalline silicate minerals can be transformed into DSi and then used by crops (Anderson et al., 1991; Gascho and Korndörfer, 1998; Wickramasinghe and Rowell, 2006; Song et al., 2013b). For most cropping soils, Si contents and stocks of plant-available Si (the Si forms immediately usable for plants including dissolved and adsorbed Si) are lower than other Si forms (Song et al., 2013b). Si forms can be transformed in different directions depending on the environmental conditions (Sommer et al., 2006). For example, LSi may be slowly dissolved and transferred to bioavailable Si for crop uptake in cropping soils without significant soluble Si input (Seyfferth et al., 2013; Song et al., 2013b). In contrast, with the increase of soluble Si fertilization, monosilicic acid may be concentrated to form polysilicic acids through three stages: a) accumulation of monosilicic acid in soil solution; b) synthesis of polysilicic acids at the expense of monosilicic acids; c) both accumulation of monosilicic acid and synthesis of polysilicic acids in soil solution (Matichenkov and Bocharnikova, 2001). Furthermore, the transformation of Si among different Si pools in cropping soils interacts with phosphorous (P) through Si–P competitive sorption (Song et al., 2011).

2.5. Agricultural effects on silicate weathering and Si balance

The weathering of silicates is the ultimate Si source for soil porewaters, rivers, and oceans, as well as a net C sink on millennial to million year timescales (Gaillardet et al., 1999; Street-Perrott and Barker, 2008). The process of Si release from silicate weathering can be significantly enhanced by agricultural activities such as crop cultivation and harvest, and fertilization (Hinsinger et al., 2001; West et al., 2002; Pierson-Wickmann et al., 2009; Fortner et al., 2012). The mechanisms of agriculturally-enhanced Si release from silicate weathering include soil acidification induced by crop cultivation and application of organic wastes (Song et al., 2011, 2013b) and fertilizers (Pierson-Wickmann et al., 2009; Fortner et al., 2012), removal of Si and base cations from crop cultivation and harvest (Hinsinger et al., 2001; Song et al., 2012a), changes of soil water dynamics through irrigation (Raymond et al., 2008; Basu et al., 2010; Struyf et al., 2010; Fortner et al., 2012), and increase of primary silicate minerals from rock powder amendments and tillage-induced soil erosion (Van Oost et al., 2005; Schuiling and Krijgsman, 2006; Larsen et al., 2014).

Silicon fertilizer application has been practiced for high Si-demanding crops such as rice and sugarcane in China, Japan, Korea, USA etc. (Savant et al., 1997b; Guntzer et al., 2012a,b). Common silicone fertilizer types include ashes and residues of blast furnaces (Guntzer et al., 2012a; Vandevenne et al., 2012). The Si fertilizer application rate depends not only on the silicon content of the fertilizer but also on the bioavailability of Si in the soils and the crop's Si demand (Wickramasinghe and Rowell, 2006; Seyfferth et al., 2013).

Enhanced silicate weathering from agricultural activities and silicon fertilizer application may partly offset the harvest and leaching losses of Si in agricultural ecosystems (Hinsinger et al., 2001; Guntzer et al., 2012a). However, they should also alter the Si cycle in agricultural ecosystems and watershed dissolved Si fluxes (Struyf et al., 2010; Carey and Fulweiler, 2012). As the biogeochemical cycle of Si may affect the C balance in agricultural ecosystems through coupled Si–C cycling, the mechanisms and management of Si–C coupling in agricultural ecosystems need to be intensively investigated.

3. Phytolith C sequestration

During their formation in plant tissues, phytoliths can occlude 1–6% of organic C (phytolith-occluded carbon, PhytOC) (Wilding et al., 1967; Harrison, 1996; Parr and Sullivan, 2005; Parr et al., 2010). PhytOC mainly consists of cellulose, simple carbohydrates and internal cytoplasmic organic cellular material depending on the deposition location of the phytolith in the plant (Krull et al., 2003; Parr and Sullivan, 2005; Carter, 2009). Although there are debates on PhytOC sources (Santos et al., 2012; Sullivan and Parr, 2012), it is commonly accepted that PhytOC is mainly of photosynthetic sources (Krull et al., 2003; Parr and Sullivan, 2005; Carter, 2009). As the production flux is higher than that of dissolution for most ecosystems, PhytOC can accumulate in soil profiles after plant decomposition and is more resistant against degradation than other soil organic carbon fractions over a millennial time scale due to silica protection (Wilding, 1967; Meunier et al., 1999; Parr and Sullivan, 2005; Strömberg, 2011). Thus, phytolith C sequestration is an important millennial scale C sink mechanism for grass-dominant ecosystems (Parr and Sullivan, 2011; Song et al., 2012b, 2013a, 2014), which contributes 15–37% of the stable soil C sink (Parr and Sullivan, 2005).

3.1. The production of PhytOC in agricultural ecosystems

The PhytOC content of crops (the amount of PhytOC in unit weight of crop biomass) depends not only on the C content of phytoliths (the amount of C in unit weight of phytoliths) (Parr and Sullivan, 2011; Zuo and Lü, 2011) but also on phytolith content of crops (Li et al., 2013). The content of PhytOC in different crop species spans a range of 1875%, from 0.04% to 0.75% of the dry crop biomass (Table 1; Parr and Sullivan, 2011; Li et al., 2013). Sugarcane and cereals such as rice, wheat and maize are rich in PhytOC, with an average PhytOC content higher than 0.20%. However, the PhytOC content also varies significantly between different cultivars (Parr and Sullivan, 2011; Li et al., 2013) and tissues (Li et al., 2013) of the same crop species.

The PhytOC production flux in agricultural ecosystems depends on the PhytOC contents of the crops and the above-ground production flux of Si-rich crop organs (SRO) (Song et al., 2013a, 2014). Although estimations of the PhytOC production flux vary substantially among different studies due to different data sources, PhytOC production flux decreases in the following order: sugarcane > rice ~ wheat ~ maize > other crops (Table 1). The high PhytOC production flux for sugarcane can be explained by its significantly high SRO production flux relative to other crops, while the low PhytOC production flux for other crops is due to their relatively low PhytOC content (Parr et al., 2009; Rajendiran et al., 2012; Song et al., 2013a, 2014).

The total PhytOC production rate for global agricultural ecosystems is 16–44 Tg CO_2 year^{-1}, more than 80% of which is contributed from cereals such as rice, wheat and maize because of their relatively large coverage and high PhytOC production flux (Table 1) (Rajendiran et al., 2012; Song et al., 2013a). However, the estimation of the PhytOC production rate for a specific crop varies significantly among different studies due to different data sources (Table 1). For example, the PhytOC production rate for wheat estimated by Parr and Sullivan (2011) is significantly higher than that estimated by Rajendiran et al. (2012) and Song et al. (2013a) as a result of both higher estimations of PhytOC contents and SRO production fluxes. More precise estimates of the PhytOC production rates for global crops are necessary.

Table 1
A comparison of the phytolith C (PhytOC) sequestration in global agricultural ecosystems and agricultural ecosystems of China and India.

Agricultural ecosystems	Area (10^6 ha)	SRO production flux (t ha^{-1} year^{-1})[a]	PhytOC content (%)	PhytOC production flux (kg CO_2 ha^{-1} year^{-1})	PhytOC production rate (Tg CO_2 year^{-1})	References
World's wheat	214	6.7	0.35 (0.11)[b]	74 (27)	15.8 (5.8)	Parr and Sullivan (2011)
	218	3.5	0.24 (0.06)[c]	31 (7)	6.6 (1.7)	Rajendiran et al. (2012)
	220	4.1	0.16 (0.08)[c]	22 (10)	4.9 (2.3)	Song et al. (2013a)
World's rice	155	14.0	0.16 (0.12)	80 (50)	12.0 (7.5)	Li et al. (2013)
	153	4.0	0.50 (0.25)	73 (37)	11.2 (5.6)	Rajendiran et al. (2012)
	164	4.8	0.25 (0.07)	40 (12)	6.6 (2.0)	Song et al. (2013a)
World's maize	145	6.0	0.22 (0.11)	49 (27)	7.2 (4.0)	Rajendiran et al. (2012)
	170	7.0	0.16 (0.05)	36 (14)	6.1 (2.5)	Song et al. (2013a)
World's sugarcane	20	40.0	0.19 (0.05)	279 (73)	5.6 (1.5)	Parr et al. (2009)
	16	25.0	0.10 (0.03)	90 (30)	1.4 (0.5)	Rajendiran et al. (2012)
	25	12.7	0.25 (0.07)	104 (29)	2.6 (0.7)	Song et al. (2013a)
World's cereals	698	5.1	0.19 (0.07)	32 (12)	22.4 (8.4)	Song et al. (2013a)
World's crops	632	4.8	0.28 (0.11)	50 (20)	31.4 (12.7)	Rajendiran et al. (2012)
	1533	5.3	0.13 (0.05)	17 (7)	26.4 (10.2)	Song et al. (2013a)
Indian crops	95	4.5	0.32 (0.12)	54 (20)	5.1 (1.9)	Rajendiran et al. (2012)
Chinese crops	135	6.1	0.16 (0.06)	36 (13)	4.9 (1.7)	Song et al. (2014)

[a] SRO production flux is the average aboveground production of Si-rich crop organs per unit area (t ha^{-1} year^{-1}).

[b] Data within parenthesis represents standard deviation.

[c] For PhytOC content estimation from data of phytolith content and C content of phytoliths, 5% was taken by Rajendiran et al. (2012), while $3 \pm 1\%$ was taken by Song et al. (2013a, 2014).

3.2. Accumulation of PhytOC in agricultural ecosystems

As the accumulation of PhytOC in cropping soils is determined by the stability and restitution of phytoliths in cropping soils, all factors that affect the restitution and stability of phytoliths will also affect the phytolith C sequestration in cropping soils (Song et al., 2012a, 2013a, 2014). After crop harvest, PhytOC produced from the root and stubble of crops is returned directly to the soil, and that produced from other parts is removed from the site (Meunier et al., 2008). A large proportion of the harvested PhytOC will reenter the cropland when the crop straws are returned to the cropland either directly by re-application of some biomass or indirectly by application of residua of biomass burning or of human and animal digestion (Vandevenne et al., 2012). Only a small part of the crop PhytOC is either consumed by human and animals or discharged into aquatic systems (Vandevenne et al., 2012). Even though some PhytOC may be finally removed from agricultural ecosystems, the largest pool of C sequestrated in phytoliths stays or is returned to soils. The storage of PhytOC in soils is long term because it is stable and more resistant against degradation than other soil organic carbon fractions (Wilding, 1967; Parr and Sullivan, 2005). Therefore, the phytolith C sink in agricultural ecosystems is better estimated from the crop PhytOC production in combination with the turnover time of phytoliths rather than from the net increase of PhytOC in soils.

3.3. Si cycle management to enhance phytolith C sequestration

Phytolith C sequestration can not only be increased by enhancing crop residua return such as partial straw retention after harvest, but also by increasing crop production and PhytOC content and their combination (Table 2).

Although increase of crop (especially cereal) production would not affect Si and PhytOC contents significantly, it would increase PhytOC production flux through enhancing crop biomass production (Song et al., 2013a). The traditional measures such as enhancing multiple cropping index (increasing the number of harvests per area within a year through an intensive crop rotation system) and scientific management of fertilizers for increasing food production may also increase PhytOC production (Song et al., 2013a). It has been demonstrated that from 1961 to 2011, traditional measures including fertilization and irrigation have increased the global cropland phytolith carbon sequestration from 8.6 Tg CO_2 year^{-1} to 26.4 Tg CO_2 year^{-1} (Song et al., 2013a). Optimization of fertilization, irrigation and cropping system may further increase both cropland phytolith C sequestration and food production.

Analysis of correlations between PhytOC content, phytolith content and Si content in crops (Li et al., 2013; Song et al., 2013a, 2014) demonstrates that PhytOC content of crops cannot only be enhanced by crop species or cultivar optimization but also by Si fertilization. For most crops the Si content in grains is much lower than that in other tissues (Li et al., 2013), therefore Si fertilization may not lead to significant Si accumulation in food products potentially decreasing food quality. However, further work such as the efficiency of amendments with Si-rich materials on increasing the PhytOC contents of different crop species and cultivars and the response of Si accumulation in food products and food quality to different Si amendments should be done to examine the rational Si fertilization flux without potential side effect.

4. Stabilization of soil organic carbon

The content and type of secondary aluminosilicates controlled by the biogeochemical Si cycle play important roles in many biogeochemical C sequestration processes including adsorption of carbon to the surface of silt and clay particles, occlusion of C in soil aggregates, and biochemical C stabilization (Fig. 2). These C sequestration processes are reviewed in the following sections.

4.1. Fixation of C on the surface of silt and clay particles

Organic C can be chemically fixed and protected by silt and clay particles through various organo-mineral associations including interactions with aluminosilicates and hydrous oxides (Hassink, 1997; Jastrow et al., 2007; Vogel et al., 2014; Wiesmeier et al., 2014). For example, complexation of organic C with aluminosilicates may occur through multivalent cation bridges between clay platelets and organic C in soils dominated by smectite and/or illite (Jastrow et al., 2007). SOC protection capacity can be defined using the association of SOC with silt and clay particles (Hassink, 1997; Puget et al., 1999).

The amount of organic C protected by silt and clay particles and the relative importance of sorption and complexation interactions for SOC fixation depend mainly on the physico-chemical characteristics of the soil minerals (Sollins et al., 1996; Baldock and Skjemstad, 2000; Vogel et al., 2014). In contrast to 1:1 clays, 2:1 clay minerals generally have a higher cation exchange capacity and a larger specific surface area, offer more sites for complexation with organics, and consequently, have a higher capacity for C protection (Sollins et al., 1996; Baldock

Table 2
Potential measures for C sequestration enhancement in agricultural ecosystems coupled with the silicon cycle (Lal, 2004a,b; Song et al., 2012a, 2013a).

Mechanisms	Measures	Comments
PhytOC regulation	Enhancing cereal production	High efficiency for all crops with low costs
	Enhancing multi- cropping index	
	Off-season cover crop growing	
	Erosion mitigation with buffer strips	
	Partial straw retention after harvest	
	Genetic engineering of plants	High efficiency in crop production with high costs
	Scientific management of fertilizers	High efficiency for all crops with high crop production
	Organic mulching and fertilization	High efficiency for cereals and sugarcane with low costs
	Silicate rock powder amendment	High efficiency for cereals and sugarcane at stable or balanced positions with low costs
	Silicon and biochar fertilization	High efficiency in acidic soils at stable or balanced positions with high costs
	Drip, furrow or sub-irrigation	High efficiency for dry crops with high crop production
Regulation of organic C stabilization	Cultivation of deep rooting crops	High efficiency for all crops with low costs
	Off-season cover crop growing	
	Erosion mitigation with buffer strips	
	Conservation tillage or no till	
	Organic mulching and fertilization	
	Silicon and biochar fertilization	High efficiency in acidic soils at stable or balanced positions with high costs
	Silicate rock powder amendment	High efficiency for cereals and sugarcane at stable or balanced positions with low costs
	Drip, furrow or sub-irrigation	High efficiency for dry crops with high crop production
Weathering regulation	Enhancing cereal production	High efficiency for all crops with low costs
	Enhancing multi-cropping index	
	Cultivation of deep rooting crops	
	Off-season cover crop growing	
	Silicate rock powder amendment	High efficiency for cereals and sugarcane at stable or balanced positions with low costs
	Drip, furrow or sub-irrigation	High efficiency for dry crops with high crop production

and Skjemstad, 2000). Agricultural activities such as crop harvest and irrigation may modify the contents and types of silt and clay particles through modifying the biogeochemical silicon cycle (Doucet et al., 2001; Lucas, 2001; Barré et al., 2009; Guntzer et al., 2012b), and thus in turn also impact C fixation on the surface of silt and clay particles.

4.2. Aggregate C sequestration in soils

Aggregation controls the processes and capacity of physical protection of SOC (Jastrow et al., 1996, 2007), and thus the accumulation of soil organic matter (SOM) in many less managed and cultivated soils (Puget et al., 1995; Franzluebbers and Arshad, 1997; Six et al., 1998,

1999; Wang et al., 2014). According to the physical size, aggregates can be divided into macroaggregates (>250 μm diameter) and micro-aggregates (20–250 μm diameter) (Fig. 2). Generally, microaggregates protect more soil organic C and are more resistant to disturbance than macroaggregates (Jastrow et al., 1996; Gale et al., 2000; Six et al., 2000, 2002).

Although many processes (e.g., soil humidity and temperature fluctuation, bioturbation, tillage and erosion) may affect aggregate C sequestration, soil clay content and type may also play an important role in SOC stabilization by affecting aggregate dynamics (Oades, 1993; Six et al., 2000, 2004; Wang et al., 2014). Physical protection of particulate organic matter within aggregates increases with increasing clay content (Franzluebbers and Arshad, 1997), and the mechanisms
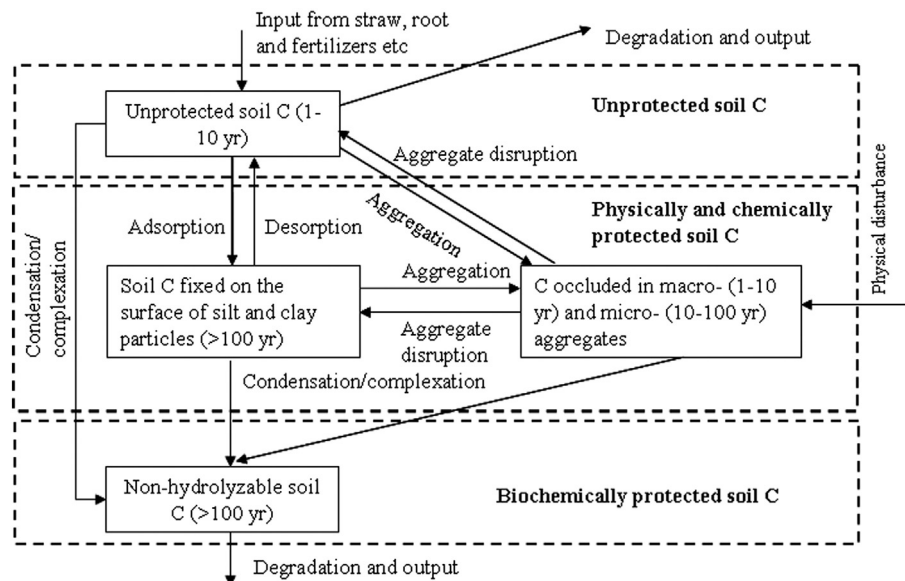

Fig. 2. Conceptual model showing protection mechanisms and turnover times of soil organic carbon (C). Numbers within parenthesis represent average turnover times for C pools. Modified from Six et al. (2002), Lützow et al. (2006), and Song et al. (2012a).

of aggregation differ among clay types (Oades and Waters, 1991; Six et al., 2002; Six and Paustian, 2014). Irrigation, silicon fertilization and other measures may affect clay content and type, thus aggregate C sequestration through modifying the biogeochemical Si cycle.

4.3. Biochemical C stabilization

Biological residue in soils are rapidly decomposed into smaller organic molecules, and either be further decomposed or condensated and polymerized to form new larger molecules depending on the soil's biotic and mineral conditions (Zech et al., 1997; Chefetz et al., 2002; Conesa et al., 2002; Sutton and Sposito, 2005; Jastrow et al., 2007). Reaction of amino compounds with quinones is considered as the main humification process for most soils (Jastrow et al., 2007). The reaction rate of amino-quinone compounds increases significantly when catalysts (e.g., amorphous silica) exist (Jastrow et al., 2007). Secondary silicate minerals with high specific surfaces (e.g., swelling phyllosilicate clays) can not only serve as catalysts of condensation but also as oxidants in the biochemical alteration process, thus control biochemical C stabilization in soils (Baldock and Skjemstad, 2000; Six et al., 2002).

The biogeochemical Si cycle in agricultural ecosystems may significantly affect the type and content of inorganic catalysts, thus biochemical C stabilization. However, further research on the effects of LSi, swelling phyllosilicate clays and other inorganic catalysts on biochemical C stabilization is required to quantify the biochemical C stabilization capacity for each cropland soil.

4.4. Si cycle management to enhance soil organic C stabilization

Traditional measures such as cultivation of deep rooting crops, growing off-season cover crops, erosion mitigation with buffer strips, conservation tillage or no till, organic mulching and fertilization, and drip irrigation may enhance accumulation of secondary silicate minerals and increase organic C stabilization in most cropping soils by modifying biogeochemical Si cycle (Lal, 2004a,b; Table 2). For example, relative to conventional tillage, conservation tillage may reduce soil erosion, enhance accumulation of secondary silicate minerals, and stabilize 100–1000 kg C ha^{-1} year^{-1} in agricultural ecosystems (Lal, 2004a). It has also been estimated that enhancing water use efficiency through modifying irrigation schedules may increase silicate weathering, enhance accumulation of secondary silicate minerals and stabilize 100–200 kg C ha^{-1} year^{-1} (Lal, 2004a). The above measures may also significantly increase crop production without obvious side effects.

5. Agricultural impacts on CO_2 consumption from silicate weathering

5.1. Silicate weathering and CO_2 consumption in croplands

Chemical weathering of fresh silicate minerals releases DSi and consumes atmospheric CO_2 and can be summarized by the following equation (Berner, 1995):

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2. \qquad (1)$$

Silicate weathering and CO_2 consumption rates are not only controlled by lithological (Amiotte Suchet et al., 2003; Hagedorn and Cartwright, 2009), climatic (Jacobson et al., 2003; Hagedorn and Cartwright, 2009) and hydrological (Maher and Chamberlain, 2014) conditions and terrestrial plant growth (Drever, 1994; Berner, 1995; Moulton and Berner, 1998; Hinsinger et al., 2001), but also affected by agricultural activities (Barnes and Raymond, 2009; Gandois et al., 2011; Fortner et al., 2012).

Crop cultivation and harvest may decrease a soil's pH and deplete the Si and base cations, thus accelerate silicate weathering leading to increased release of DSi and base cations which consume CO_2 (Hinsinger et al., 2001; Song et al., 2012a). For example, using basalt powder in the absence or presence of lupin (*Lupinus lutens*), maize (*Zea mays*) and other plants, Hinsinger et al. (2001) found that the dissolution of the basalt powder was significantly accelerated by all four plants by a factor between 1 and 5, but the weathering rate of the basalt powder was higher for the Si-accumulator crop maize. The former can be explained by pH decrease resulting from the crops' organic acid secretions and the related soil CO_2 buildup (Berner, 1992, 1997; Hinsinger et al., 2001), while the latter is related to the differences in the crops' Si accumulating efficacies (Savant et al., 1997a,b; Hinsinger et al., 2001). However, the long-term trend of silicate weathering and CO_2 consumption in croplands remains unclear.

Agricultural activities may also cause hydrological changes and thus CO_2 consumption from silicate weathering (Raymond et al., 2008; Basu et al., 2010; Fortner et al., 2012). Total discharge and DSi yields in rivers of Iowa were reported to increase by 40–100% related to changes in the seasonal–annual vegetation (Zhang and Schilling, 2006). However, Struyf et al. (2010) and Fortner et al. (2012) revealed that sustained cultivation in watersheds caused a 50–60% decline in baseflow Si delivery. Shifting the land use type in a watershed may alter the timing and frequency of flow events, but it shouldn't alter the total discharge volume unless it would also induce significant changes in the total evapotranspiration. More work is required to quantify the effects of land use changes on hydrology and silicate weathering over varying time scales and under different lithological and cultivation conditions.

Agrochemicals (e.g., ammonitrates) and organic fertilizers (e.g., urea) produce protons, lower the soil pH and thus, increase silicate weathering (Barnes and Raymond, 2009; Guo et al., 2010; Fortner et al., 2012). It was shown that between 1979 and 2009, silicate weathering from application of nitrogenous fertilizers produced about 8% of all DSi generated from the Ohio–Tennessee River Basin (Fortner et al., 2012). However, the fertilization-driven silicate weathering does not consume CO_2 (Barnes and Raymond, 2009; Pierson-Wickmann et al., 2009; Gandois et al., 2011; Fortner et al., 2012).

Furthermore, tillage may erode surface soils, expose more fresh primary silicate minerals and thus, accelerate silicate weathering and CO_2 consumption in uplands (Van Oost et al., 2005; Larsen et al., 2014). However, the effect of soil erosion from tillage on CO_2 consumption during silicate weathering has not been fully investigated.

5.2. Si cycle management to enhance weathering C sequestration

Traditional measures such as enhancing cereal production, enhancing multiple cropping index, cultivation of deep rooting crops, off-season cover crop growing, and drip or sub-irrigation can not only increase food production, but also enhance Si release and CO_2 consumption through accelerating silicate weathering (Table 2). Although the mechanisms of enhanced silicate weathering related to these measures can be explained by soil acidification (Berner, 1992, 1997; Hinsinger et al., 2001), crop Si uptake (Savant et al., 1997a,b; Hinsinger et al., 2001) and hydrological changes (Raymond et al., 2008; Basu et al., 2010; Fortner et al., 2012), the potential of these measures in enhancing weathering C sequestration needs to be fully quantified.

Other measures such as olivine and basalt powder amendments to soils threatened by acidification have been shown to be highly efficient in increasing C sequestration associated with silicate weathering (Schuiling and Krijgsman, 2006; Hartmann and Kempe, 2008). For example, Schuiling and Krijgsman (2006) estimated that a 0.4 cm layer of olivine may neutralize about 5 kg of CO_2. However, it has to be noted that the potential of olivine/silicates applications to increase silicate weathering is still theoretical at best. Furthermore, as weathering of Ca- and Mg- silicate rocks such as olivine may result in soil heavy metal (e.g., Ni) accumulation, and soil and water pH enhancement (Schuiling and Krijgsman, 2006; Hartmann and Kempe, 2008), the maximum amendment amount of silicate rock powder in

acidic cropping soils should be set to avoid adverse food and environmental consequences.

6. Geomorphic controls on feedbacks of C sequestration processes

Most eroded soils from uplands of agricultural regions finally deposit in lowland positions (Montgomery, 2007; Quinton et al., 2010). The erosion and deposition of soils lead to the redistribution of soils and can change the C balance through affecting the weathering process (Larsen et al., 2014) and profile PhytOC and SOC distribution (Doetterl et al., 2012; Chaopricha and Marín-Spiotta, 2014; Wang et al., 2014) at different geomorphic positions (Fig. 3).

Under stable or balanced soil conditions, crop growth and harvest together with silicate amendment accelerate silicate weathering and CO_2 consumption, increase silt plus clay contents, and help aggregation, and thus increase the accumulation of SOC (Fig. 3A). However, crop growth and harvest may increase or decrease soil PhytOC accumulation depending on the ratio of crop harvest and residue return. Organic amendments may increase the accumulation of phytoliths in soils as well as aggregation, and thus, increase organic C sequestration.

Tillage may erode soil and change Si and C balance in soil profiles (Fig. 3B). Under erosion-limited conditions such as warm and humic plains with only gentle slopes, tillage accelerates silicate weathering and CO_2 consumption by removing highly-weathered soil minerals and supplying more fresh primary silicate minerals. However, under most chemical weathering-limited conditions such as mountainous or hilly areas with steep slopes, tillage decelerates silicate weathering and CO_2 consumption by decreasing the mineral-water reaction time. The erosion process also removes significant amounts of organic C, silts plus clays, destabilizes soil aggregates, and thus, reduces organic C stabilization in soil profiles.

In contrast, deposition of soils eroded from uplands may either decelerate or accelerate silicate weathering and CO_2 consumption depending on climatic and topological conditions (Fig. 3C). It also buries significant amounts of organic C, silts plus clays, stabilizes soil aggregates, thus, increases C stabilization in soil profiles.

The net effect of soil erosion on C balance may vary with different climatic, lithological, topological and type of tillage and soil conditions during tillage. Further assessment of soil erosion on C balance under different climatic, lithological and topological conditions is necessary to improve agricultural C management.

7. Conclusions

Silicon accumulates in many major crops and may increase crop production through enhancing crops' resistance to many biotic and abiotic stresses. Global cultivation and harvest of major crops may change the global biogeochemical Si cycle. Carbon sequestration in agricultural ecosystems is coupled with the Si cycle through many biogeochemical processes such as dynamics of phytoliths and aggregates, and silicate weathering at different time-scales. Strategic management of the biogeochemical Si cycle in agricultural ecosystems
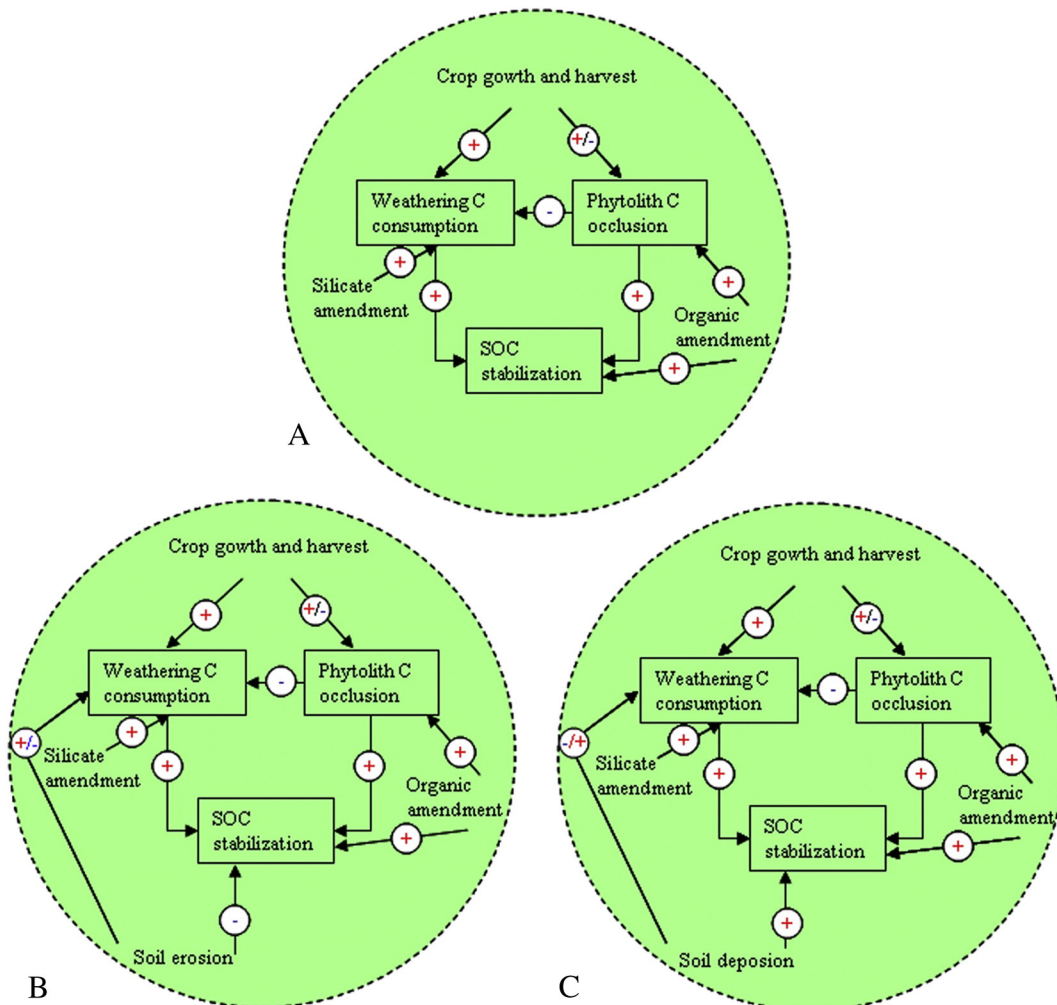

Fig. 3. Feedbacks of C sequestration in agricultural ecosystems of different geomorphic positions. A, Stable or balanced positions. B, Eroding positions. C, Depositional positions. "+" represents positive feedback, "+/−" represents positive or negative feedback depending on management practices, "−" represents negative feedback.

offers a new possibility to enhance C sequestration because Si-related C sinks are more stable than other C sinks. Silicate rock powder amendment and traditional measures for increasing food production such as off-season cover crop growing and irrigation are potential strategies to enhance C sequestration through modifying biogeochemical Si cycle in agricultural ecosystems. However, there are some areas to be further investigated:

(1) The relative contribution of silicate weathering, and dissolution of phytoliths and other amorphous Si forms to the soil bioavailable Si pool in different agricultural ecosystems needs to be quantified.

(2) The relative importance of processes in coupled biogeochemical cycles of Si and C and their feedbacks should be compared between different agricultural ecosystems. More field experiments under different climatic, topological, soil and crop conditions should be specifically designed to thoroughly examine the effects of agricultural management measures on the Si cycle and C sequestration.

(3) What is the potential and cost of each management measure to enhance C sequestration? How can different measures be combined to more efficiently enhance C sequestration? These questions deserve intensive investigation to guide the manipulation of C sequestration in agricultural ecosystems.

(4) Carbon sequestration coupled with the Si cycle in cropping soils should be incorporated into global C cycle models to better understand the effect of agricultural management on global C sequestration and climate change.

Acknowledgments

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