Quantification of distinct phytolith pools in a perhydrated Andosol

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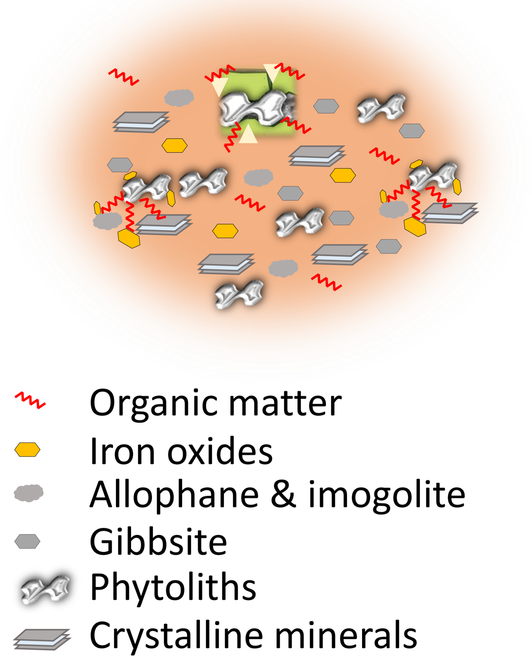
Silicon (Si) is the second most abundant element of the earth crust. The Si cycle strongly depends on the bio-cycling of Si by plants. Plants roots absorb the dissolved silicon (DSi) present in the soil solution and accumulate it into amorphous silica bodies called **phytoliths (PhSi)**. Once plant debris return to soil, **PhSi may constitute an important silica pool in soil**. PhSi **strongly contributes to the DSi pool**; especially in desilicated weathered soils. To understand the soil-plant Si cycle it is thus primordial to quantify the PhSi pool in the soil.
However, **quantification methods are still not very well defined** especially in soils in which pedogenic amorphous silica pools are abundant.



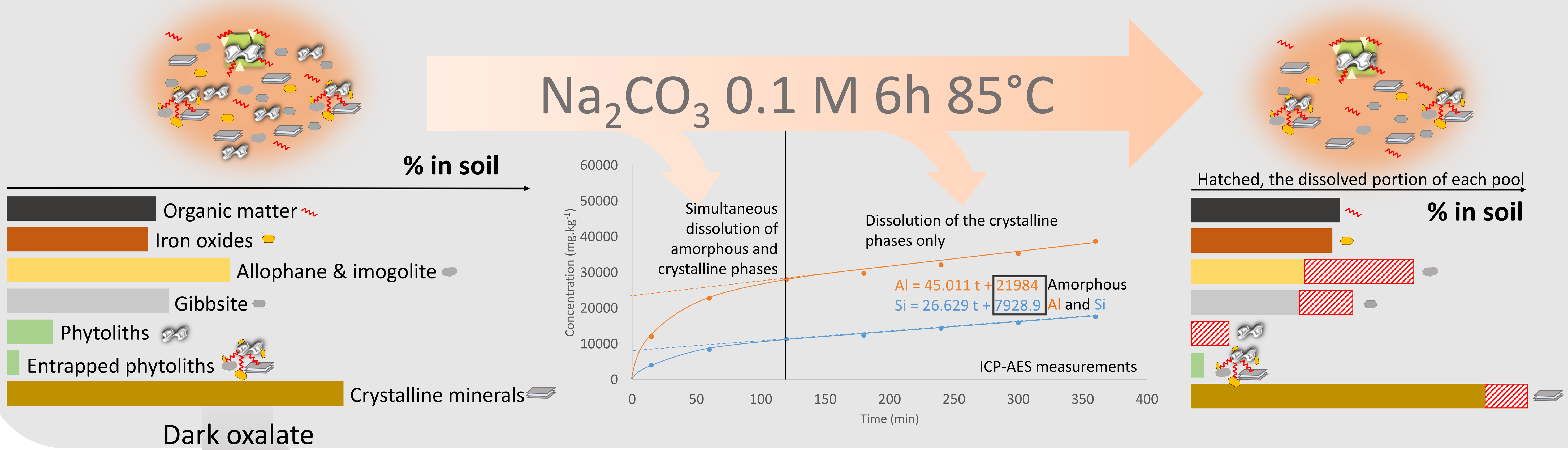
Material

The studied soil comes from the Basse-Terre island in Guadeloupe (16°N, 61°W). MAP is 4270 mm. The soil is a perhydrated Andosol with high organic matter content and secondary minerals typical of Andosol. DRX analyses allowed to identify pyroxene and plagioclase as the main primary minerals while halloysite and gibbsite are the main crystalline secondary minerals. Volcanic glasses are absent in the studied soil. Allophane and imogolite content is 8.0 % and ferrihydrite content is 2.6%.

Method

As phytoliths are solubilized under alkaline conditions, chemical extraction technics use alkaline reagents (mainly NaOH 0.5 M and Na_2CO_3 0.1 M). Alkaline reagents quickly dissolve phytoliths, and part of allophane and imogolite pools. They also dissolve crystalline minerals slowly and continuously. The time course extraction method developed by DeMaster (1981)[1] allows to differentiate amorphous from crystalline Si pools by extrapolating the linear part of the extraction (after 2h) to time zero.
Quantification of phytoliths in volcanic soils is a real challenge as pedogenic and lithogenic amorphous minerals overlap the dissolution of phytolith with alkaline reagents.
Here we propose a method with successive pretreatments that eliminate sequentially different pools in order to better understand the process of alkaline extractions.

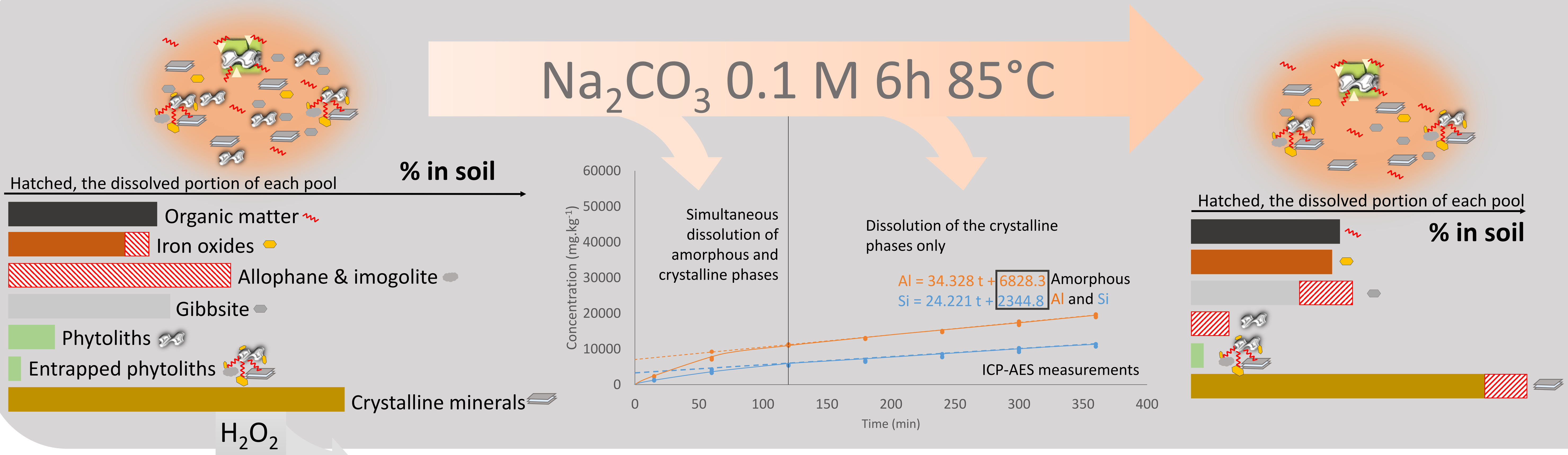
Method 1 No pretreatment



Amorphous Al (AAl) corresponds to the dissolution of a part of allophane, imogolite and poorly crystalline $Al(OH)_3$ if present or gibbsite. Amorphous Si (ASi) corresponds to the dissolution of a part of allophane, imogolite and phytoliths. It is difficult to discern the part of the amorphous Si that comes from phytoliths. The use of the Si:Al ratio is difficult in that case as poorly crystalline $Al(OH)_3$ or gibbsite (purely aluminous minerals) could also dissolve.

Dark oxalate
4h
Allophane Imogolite Ferrihydrite

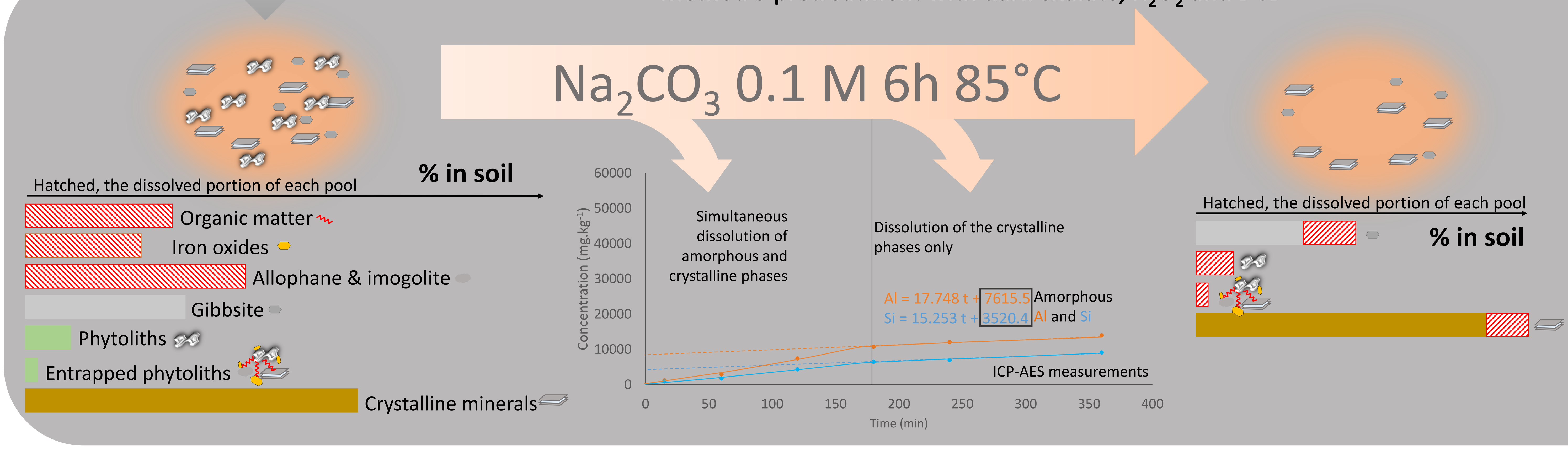
Method 2 pretreatment with dark oxalate



AAl corresponds to the dissolution of poorly crystalline $Al(OH)_3$ if present or gibbsite as allophane and imogolite have been removed from the sample with a dark oxalate extraction. ASi corresponds to the dissolution of phytoliths. In that case, the phytolith pool can be easily estimated as it corresponds to the ASi pool.

H_2O_2
DCB
Organic matter
Iron oxides

Method 3 pretreatment with dark oxalate, H_2O_2 and DCB



Here, in addition to allophane and imogolite, crystalline iron oxides and organic matter are removed from the sample with H_2O_2 and DCB treatments. These two pretreatments aim to destroy aggregative components. Both the AAl and ASi pools increased compared to AAl and ASi obtained from method 2. This suggests that the removal of aggregative constituents liberates phytoliths that were not dissolved whithout H_2O_2 and DCB treatments.

Concluding remarks

In the Andosol, allophane, imogolite and microaggregates could make the quantification of the PhSi pool difficult. We propose a new methodology to quantify the free phytolith pool that readily contributes to the soil-plant Si cycle and the total phytolith pool. Moreover, our results, particularly the atomic Si:Al ratio, show that the Na_2CO_3 0.1 M solution dissolves Al compounds not involved in Al-humus, allophane and imogolite. These Al compounds might best refer to a continuum extending from poorly crystalline $Al(OH)_3$ to clay-sized gibbsite. These compounds, such as phytoliths, readily dissolve in the Na_2CO_3 solution.

Acknowledgements

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[1]DeMaster, D. J. (1981) *Geochimica et Cosmochimica acta*, *45*(10), 1715-1732