

2.7.P13

Surface properties, solubility and dissolution kinetics of phytoliths, from bamboos of Réunion Island

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Although phytoliths, constituted mainly by micrometric opal, have an important control on silicon cycle in superficial continental environments, their physico-chemical properties and their reactivity in solution are still poorly known. The aim of this work is to determine the solubility and dissolution kinetics of bamboo phytoliths from Réunion Island and to characterize their surface properties via electrokinetics measurements, potentiometric titration, and metals adsorption experiments at ambient temperature in a wide range of pH (from 1 to 11).

The solubility product of phytoliths ($pK_{sp} = 2.74$) at 25°C is equal to that of vitreous silica and 17 times higher than that of quartz.

Electrophoretic measurements allowed to determine phytoliths $pH_{IEP} = 1.2 \pm 0.1$ which is comparable with that of quartz but lower than that of amorphous silica.

Phytoliths dissolution kinetics, measured in mixed-flow reactors at far from equilibrium conditions, is intermediate between that of quartz and vitreous silica (see Figure). Similar to quartz and amorphous silica, the dissolution rate dependence on pH ($pH \geq 3$) can be modeled within the concept of surface coordination theory using the equation:

$$R = 10^{-6.5} * \{>SiOH^0\} + 10^{2.9} * \{>SiO^-\}^{1.7}$$

It follows from the results of this study that phytoliths dissolution rate exhibits a minimum at $pH \sim 3$. This can explain their good preservation in the acidic soil horizons of Réunion Island. Further study of the physico-chemical properties and reactivity of phytoliths of different origins should improve our knowledge of the biogeochemical cycle of silicon in various terrestrial environments.

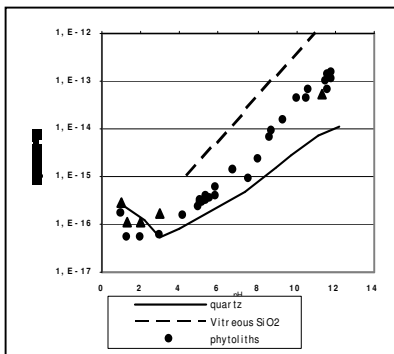


Fig. Dissolution rates of phytoliths as a function of pH in mixed-flow reactors at 25°C

2.7.P14

Chemical evidence for dairying at the Neolithic lake-shore settlement Arbon Bleiche 3, Switzerland

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The chemistry of organic residues from potsherds was used to get further insight into the dietary trends at the Constance lake-shore Neolithic (3384-3370 BC) settlement of Arbon Bleiche 3, Switzerland. The approach includes stable carbon and nitrogen isotope composition ($\delta^{13}C$, $\delta^{15}N$) of the bulk organic residues, and the molecular and carbon isotopic characterization of the organic-solvent extracted individual fatty acids (FA). The results are compared with modern equivalents of animal and vegetable fats, which may have been consumed in a mixed ecology community with hunting, fishing, gatherer, breeder, shepherd, and agrarian activities. The covariations of the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ and $\delta^{13}C_{18:1}$ vs. $\delta^{13}C_{18:0}$ serve to distinguish between animal fats preserved in archaeological vessels [1].

The total nitrogen content (~15 wt%) and C/N ratios (5.7 to 19) of the organic residues are in the range of cooked/altered protein-rich food. The variations of the $\delta^{13}C$ and $\delta^{15}N$ values ($-26.1 \pm 0.8\text{‰}$ and $+3.7 \pm 1.8\text{‰}$, respectively) within the range expected for degraded animal and plant tissues ($+ \sim 3\text{‰}$) in a terrestrial C_3 -photosynthetic environment, are consistent with the archaeological evidence of animals, whose subsistence was mainly based on C_3 plants. The fatty acid composition (C_9 to C_{24} range, maximizing at C_{14} and C_{16}) and palmitic ($C_{16:0}$) vs. stearic acid ($C_{18:0}$) covariation point to degraded fat of animal rather than plant origin. The relatively high concentration of $C_{12:0}$, $C_{14:0}$, $C_{15:0}$ and $C_{17:0}$ fatty acids in many residues suggest storage and cooking of dairying products. Most samples plot in the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ and $\delta^{13}C_{18:1}$ vs. $\delta^{13}C_{18:0}$ fields of ruminant milk, and young suckling calf/lamb and pig adipose. These results, combined with the predominance of found bones from very young suckling calves or senile (non lactating) cows, indicate high production and consumption of milk by Neolithic Swiss at lake Constance.

References

- [1] Evershed R.P., Dudd S.N., Charters S., Mottram H., Stott A.W., Raven A., van Bergen P.F., and Bland H.A. (1997) *Phil Trans R Soc* **354**, 19-31