New insights into Monte Carlo simulation of borosilicate glass aqueous alteration

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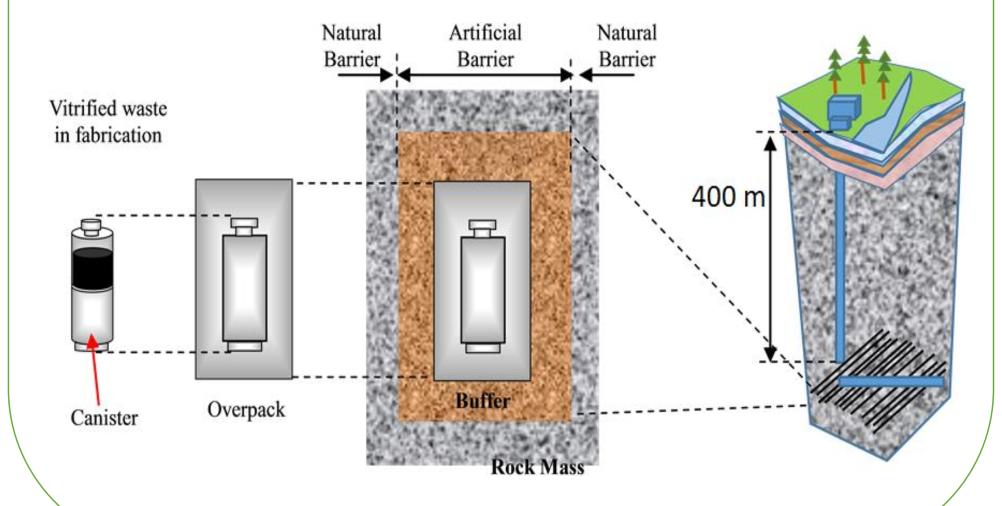
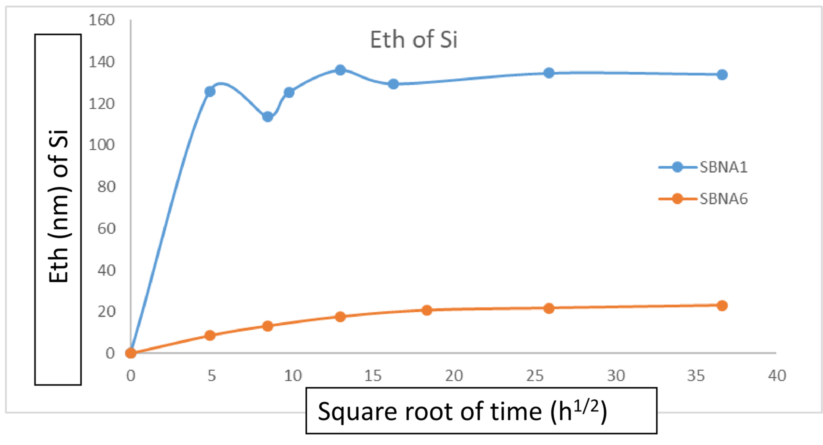
Global context

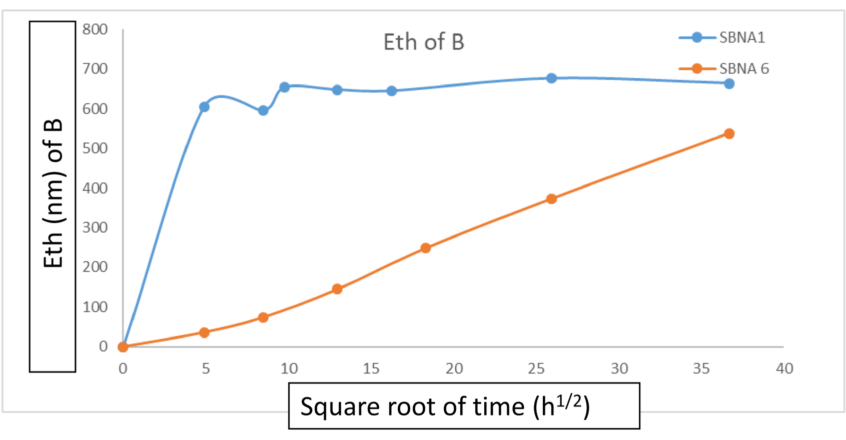
One of the widely accepted ways for the long term storage and isolation of HLW from biosphere, is their vitrification in a borosilicate glass matrix followed by disposal on a geological time scale. Hence the study of glass alteration is of utmost importance to assess the long term stability of these glasses.



EXPERIMENTAL OBSERVATIONS

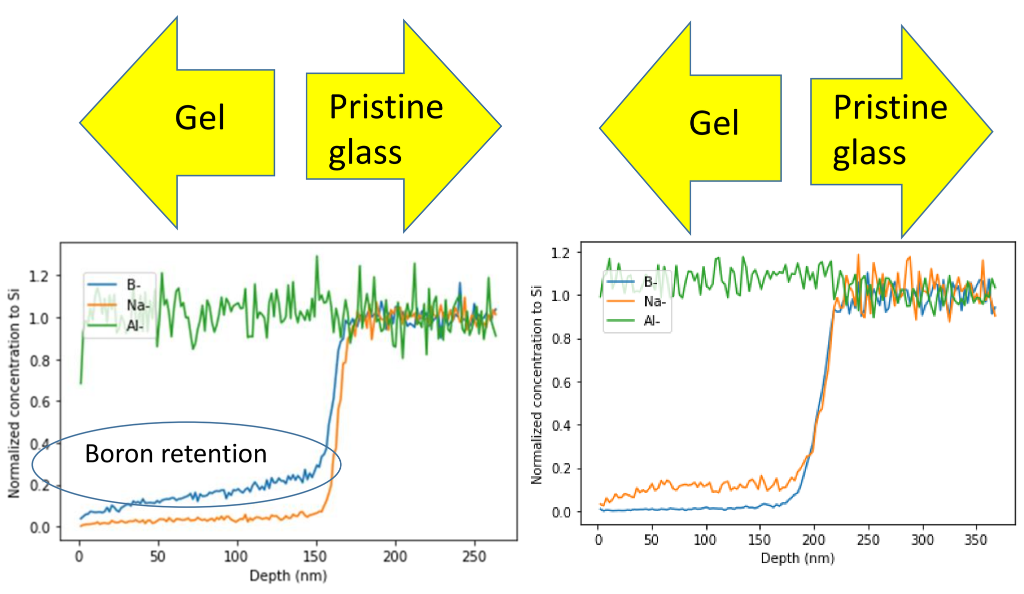
(mol%)	SiO_2	B_2O_3	Na_2O	Al_2O_3
SBNA1	63.0	18.7	17.3	1.0
SBNA6	66.8	15.9	11.3	6.0





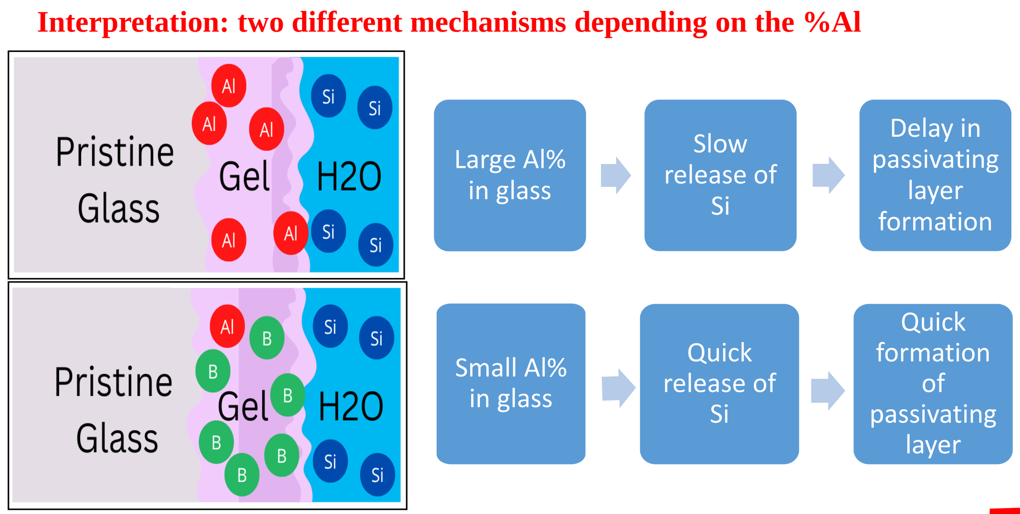
Long term dissolution of Si and B from SBNA series of glasses (glass powders) recorded (ICP-AES) with respect to the square root of time (in hours)

- For SBNA1, the release of Si is quick (due to low Al%, the hydrolysis energy around Si decreases [K. Damodaran]) and stops rapidly. The release of boron stops also rapidly. It is suspected that a passivating layer enriched with Si is formed.
- For SBNA6, the release of Si is slow due to the higher Al% and the rate of release of boron does not slow down. The formation of the passivating layer is slower.



ToF-SIMS analysis of SBNA1 (left) and SBNA6 (right) glass altered coupon.
Alteration ran for 2 months in a Si saturated solution at 90°C pH 9 in the same conditions as the glass powders.
Boron retention is observed for SBNA1 and not for SBNA6, confirming the quicker formation of the passivating layer for the SBNA1 glass.

Interpretation: two different mechanisms depending on the %Al



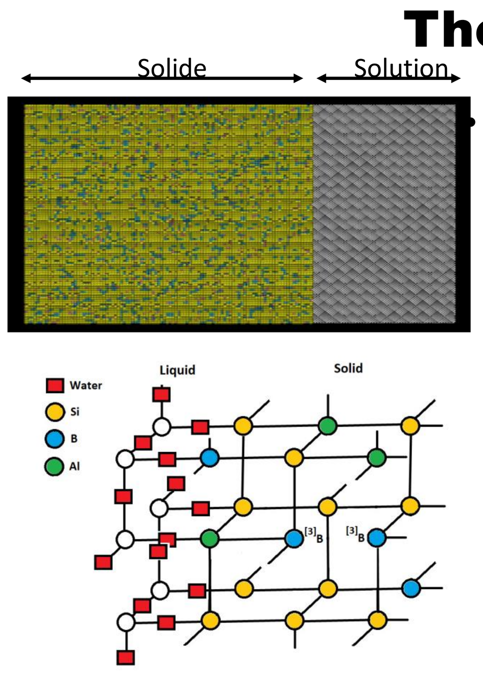
Objective

Understanding the origin of residual alteration rate for nuclear glasses subjected to aqueous corrosion

- First axis: development of a new Monte-Carlo method to better simulate the alteration gel formation and unravel the underlying mechanisms of the residual rate.
- Second axis : development of classical force fields for molecular dynamics (MD) simulations to represent (SiO_2-Al_2O_3-CaO)+(B_2O_3+H_2O) systems. Investigation of boron diffusion in a simplified alteration gel.
- Third axis : Experiments on a series of SiO_2-Al_2O_3-B_2O_3-Na_2O glasses to characterize the alteration gel (gel ripening, porosity …).

The three axis will be coupled to reach the objective

The new Monte-Carlo method



Characteristics of the Monte Carlo network:

- Two interconnected networks for the solid and the liquid (in the previous MC method, only one network was used)
- the diffusion of water inside the "solid network" can be simulated
- the ripening of the gel can be simulated (the diffusion of voids on the solid network is implemented)

- Composition treated: SiO_2-Al_2O_3-B_2O_3-Na_2O glass composition.

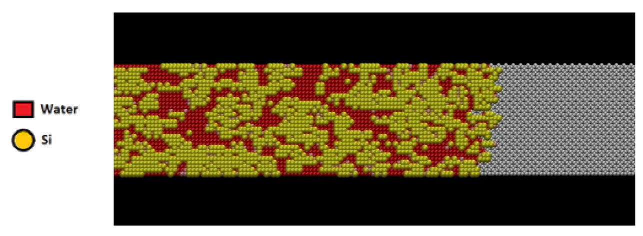
Mechanisms involved

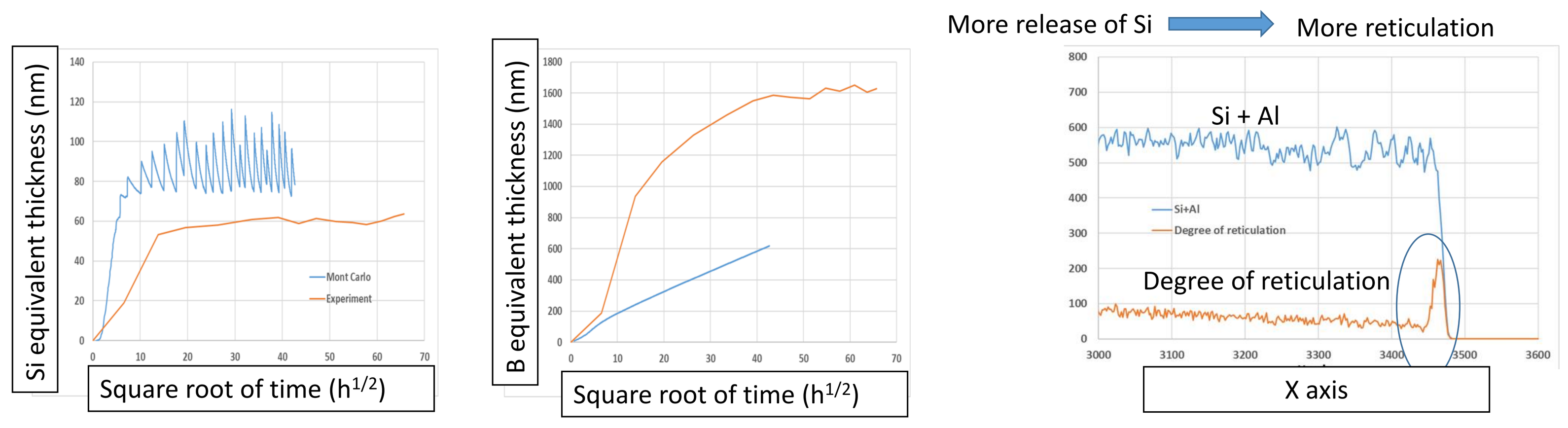
- Diffusion of water
- Bond breakage on solid network
- Reformation of the chemical bonds on solid network
- Si/Al can be conditionally re-deposited on the glass surface
- Migration of vacancies into the solid network (occupied or no by water molecules)
- Removal of isolated clusters in solution

Simulation of the formation of the alteration gel

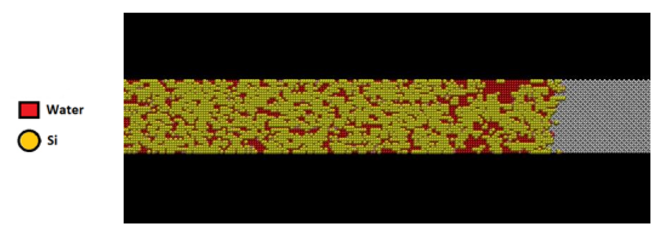
Reproduction of the asymptotic value for the Si and B equivalent thickness in comparision with experiments

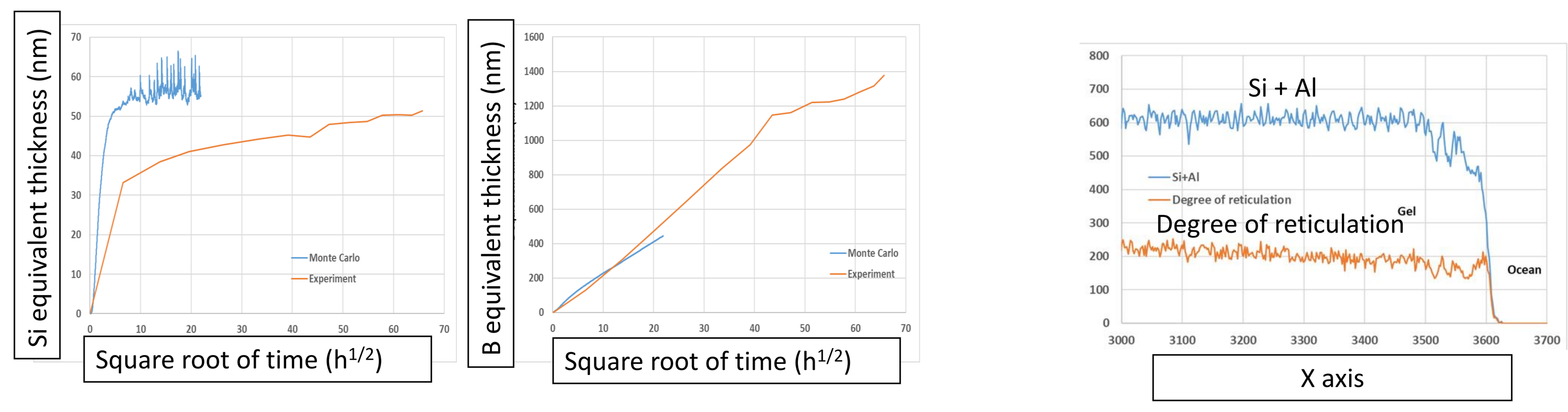
(mol %)	SiO_2	B_2O_3	Na_2O	Al_2O_3
SBNA3.5	60.5	20.1	15.9	3.5



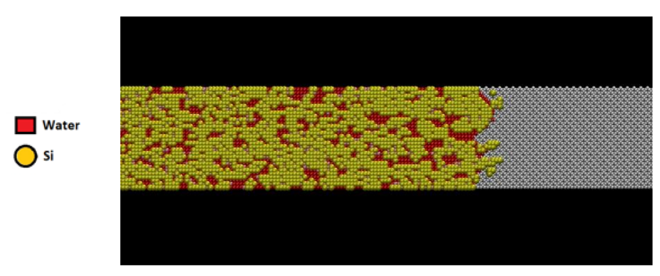


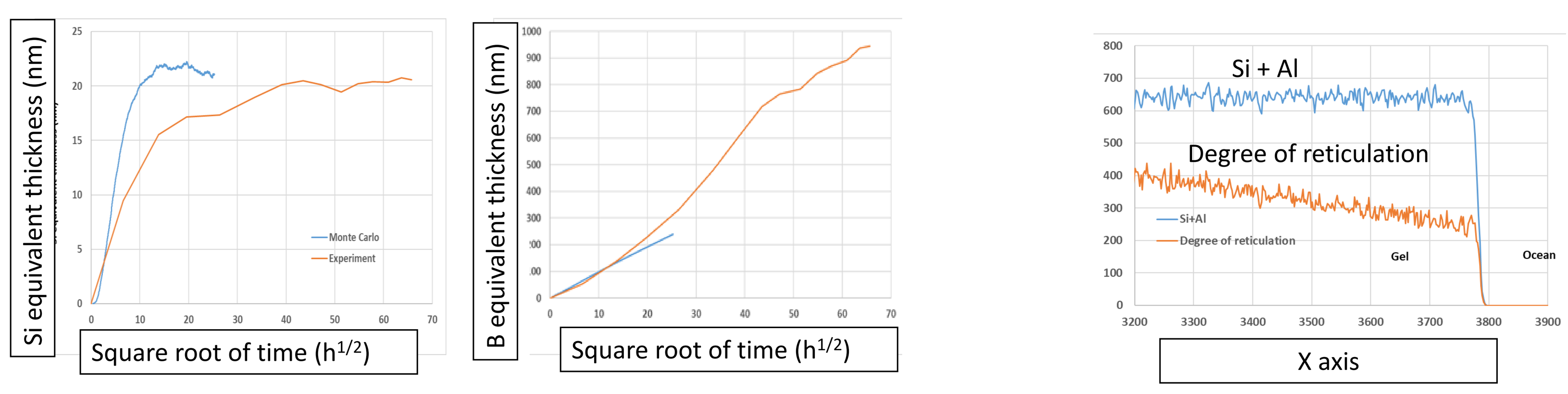
(mol %)	SiO_2	B_2O_3	Na_2O	Al_2O_3
SBNA4	64.9	17.3	13.7	4.1





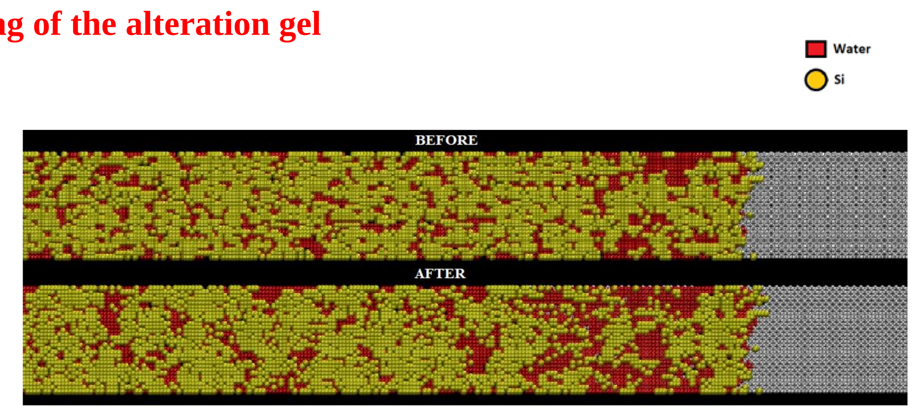
(mol %)	SiO_2	B_2O_3	Na_2O	Al_2O_3
SBNA6	66.8	15.9	11.3	6





Simulation of the ripening of the alteration gel

- The simulation of the ripening is performed after the simulation of the formation of the gel
- During ripening, large pores are formed
- *Perspectives: The gel morphology will be completly investigated (pore size, channels, bottlenecks …)*



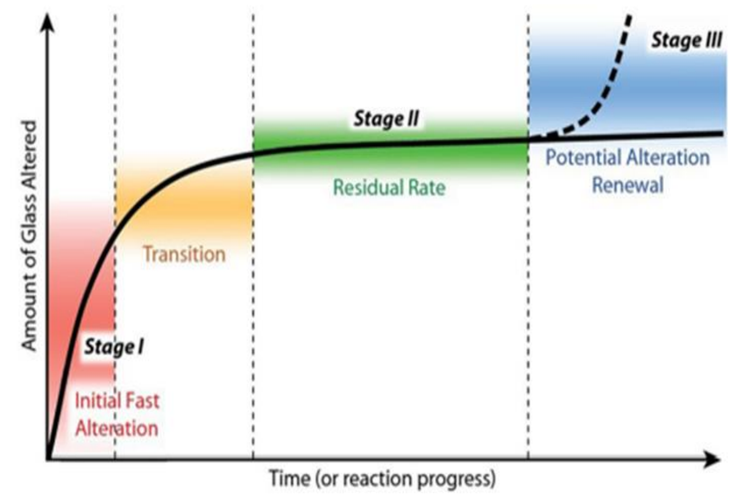
Snapshot of MC simulation for SBNA4 glass before and after maturation

Interpretation coming from Monte Carlo

- Quick release of Si: formation of an external layer enriched in Si (K. Damodaran's result)
- Slow release of Si: formation of a more reticulated external layer with no Si enrichment (this result)

Scientific context

The glass alteration over time is divided into three stage [Vienna et al].
Stage I is defined as congruent glass dissolution at a high rate in effectively dilute solution conditions. As the ion concentrations in solution increase, the glass alteration behavior undergoes a transition to Stage II.
During Stage II, a multitude of simultaneous mechanisms combine to result in a slow "residual" rate.
During Stage III, renewal of the alteration can occur because of the formation of secondary phases.



There is no clear consensus about the underlying mechanisms controlling the residual rate regime. In particular, the role of boron can be more complex than we thought. It is suspected that boron retention in the gel under certain conditions can be tied to the decrease of the glass dissolution rate.

CONCLUSIONS

- Case 1: When a large quantity of Si (glasses with a low %Al) is released in solution: it is proposed that an external layer enriched in Si forms on the gel
- Case 2: When a lower quantity of Si (glasses with a larger %Al) is released in solution: it is proposed that a more reticulated external layer forms
- These different layers could explain why the boron release stops (case 1) or no (case 2)
- ToF SIMS confirms the boron retention in case 1 (SBNA1 glass)
- These conclusions are based on a coupling between experiments and Monte Carlo

PERSPECTIVES

- By coupling Monte Carlo, classical MD and experiments, we aspire to better understand boron diffusion in the gel and some basic mechanisms that control the residual rate

* K. Damodaran "Insights into the mechanisms controlling the dissolution of alumino-borosilicate glass and development of a new Monte Carlo model ", PhD, Université de Montpellier, 2022.

*Vienna, J. D., Ryan, J. V., Gin, S. & Inagaki, Y. Current understanding and remaining challenges in modeling long-term degradation of borosilicate nuclear waste glasses. Int. J. Appl. Glass Sci. 4, 283–294 (2013).