Implications of sepiolite dehydration for earthquake nucleation in the Galera Fault Zone: A thermodynamic approach

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ABSTRACT

A new thermodynamic model for the Mg-phyllosilicate sepiolite was developed and used to calculate its P-T stability conditions and water content for different bulk rock compositions. The standard-state thermodynamic properties, entropy (S°) and enthalpy (H°), were initially estimated by oxide summation taking into account the different entropic and enthalpic contributions of the three types of water in sepiolite: zeolitic water, bound water, and structural OH groups. The starting model was then refined with experimental data. The dehydration process follows a step function that allowed us to define "end-members" with decreasing hydration states in a theoretical solid solution.

The stability field of sepiolite is ultimately limited by the reaction sepiolite = talc + quartz + H₂O, which is located at about 325 °C at 1–500 MPa. The large thermodynamic stability field of this clay mineral suggests that it could control the mechanical behaviour of crustal faults to 325 °C. The refined model was then applied to the natural case of the Galera Fault Zone (SE Spain) using thermogravimetric analysis and X-ray fluorescence data of the bulk rock composition of the fault core gouge, which is mainly composed of sepiolite. The dehydration of sepiolite at T < 300 °C is modest compared to that occurring during its breakdown, where 62% of water molecules leave the structure to form the association talc + quartz + H₂O; a reaction that also involves a reduction of around 31% of the original solid volume. These significant hydration and volume changes of sepiolite can have important implications on the strength and mechanical stability of the Galera Fault and other sepiolite-bearing gouges. We compare triaxial friction experiments on the natural sepiolite-rich gouge with a synthetic gouge to estimate strength changes on the gouge with depth. The synthetic gouge represents the breakdown association above 325 °C, and was constructed following the mineral phases predicted by the thermodynamic model (93 wt% talc and 7 wt% quartz). The contrasting frictional strength and mechanical stability of sepiolite in comparison to talc could be one of the causes of fault instability and earthquake nucleation seen to be concentrated in the upper 13 km of the Galera Fault.

1. Introduction

Phyllosilicates are abundantly found within active fault systems, where their crystallographic structure retains large amounts of water (Haines and van der Pluijm, 2012; Morton et al., 2012; Richard et al., 2014; Schleicher et al., 2012; Yalçin and Bozkaya, 2004). The presence of water, both within the crystals and on their main cleavage planes, often results in the low strength of clay-rich fault zones (Lockner et al., 2011; Schleicher et al., 2013). By facilitating slip and distributing water within active faults, clay minerals play an important role in the mechanics of earthquakes.

Clay mineral dehydration in active fault systems requires a complex reorganisation of water molecules. Controlled humidity chamber experiments have shown that water layers in smectite occur at seismogenic depths, and that humidity in this context also affects particle orientation (Schleicher et al., 2013). The hydration state and particle orientation of clay minerals in active fault systems suggest greater mobility of the particles, which has important effects on frictional strength of fault gouges (Moore and Lockner, 2007; Schleicher et al., 2013). Furthermore, numerical simulations of pore pressure within

fault zones have linked the onset of dehydration reactions in fault systems to instabilities on the fault plane. This leads to a transient acceleration of the fault motion, which stops when the reaction is finished but that can strongly modify the nucleation of unstable slip (Brantut et al., 2011). The evolution of fault strength and its relation to the seismic cycle requires the observation of natural systems to evaluate the extent of competing mechanisms such as fracturing and healing. These mechanisms are strongly dependent on the geological context, including the mineralogy and fluid flow in the area, which consequently are controlling factors on important processes within fault zones such as creep, mass transfer and pressure solution (Gratier, 2011).

Fibrous clay minerals commonly occur within fracture and fault zones (Post and Crawford, 2007; Sánchez-Roa et al., 2016), occasionally constituting the major portion of fault gouges in active faults. Thus, the study of the role of fibrous phyllosilicates becomes crucial to understand their relationship to earthquake dynamics. Sepiolite is a fibrous clay mineral that can occur as a product of weathering of ophiolitic bodies (Gleeson et al., 2004; Ratié et al., 2015) and related to other Mg-rich minerals with important roles in fault stability such as saponite, minerals from the serpentine group, and talc (Manning, 1995; Yalçin and Bozkaya, 2004). Sepiolite is found associated with fault zones and fault planes (Haines and van der Pluijm, 2012; Sánchez-Roa et al., 2016). Therefore, the study and modelling of the hydration state, mineral reactions, as well as the thermodynamic and mechanical stability of sepiolite are key steps towards understanding the mechanical behaviour of sepiolite-rich fault gouges.

Sepiolite is composed of continuous silica tetrahedral sheets with the apical oxygen periodically inverted and a discontinuous octahedral layer between them (García-Romero and Suárez, 2013). Due to these periodical inversions, sepiolite has a fibrous morphology and channels containing H_2O molecules. These channels can also accommodate some organic molecules and exchangeable cations (which are not bound to the structure) such as Na^+, K^+, and Ca^{2+} (Krekeler and Guggenheim, 2008). Sepiolite is a hydrated Mg-rich fibrous phyllosilicate with ideal formula: $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4 \cdot 8(H_2O)$. It contains three crystal-chemical states of water molecules: zeolitic water in the channels; bounded water completing the coordination of Mg^{+2} atoms in the edges of the octahedral layers; and hydroxyl groups (OH^-) in the octahedral layer (Brauner and Preisinger, 1956). Experimental data has shown that dehydration of sepiolite consists of various stages containing step functions (Nagata et al., 1974; Post et al., 2007). First, most of the zeolitic water is lost when heated to 117 °C or at room temperature under a vacuum of 1.33×10^{-4} Pa. No change in the unit cell had been recognised until Rietveld refinements of temperature-resolved synchrotron powder X-ray diffraction data showed a slight decrease in the a (decrease of ~1.2%) and c (decrease of ~0.2%) unit cell parameters during this stage (Post et al., 2007). This structure corresponds to the sepiolite-$4H_2O$ end-member. The loss of the bounded water takes place in two subsequent stages that are accompanied by the folding of the sepiolite structure and formation of the experimentally achieved sepiolite-$2H_2O$ and sepiolite-$0H_2O$ (a high temperature structure that retains the hydroxyl groups) (Nagata et al., 1974; Post et al., 2007).

The presence of sepiolite in the fault gouge of active faults and its hydration properties lead us to seek appropriate tools to discover the way sepiolite behaves under changing chemical and physical conditions. Currently there is a shortage of data on the evolution of this fibrous clay mineral in nature, including sepiolite interactions and compatibility relations with other phases in a wide range of pressure and temperature conditions. To date, progress has been made to estimate the thermodynamic properties of fully hydrated and dehydrated sepiolite (Wolery and Jove-Colon, 2004; Ogorodova et al., 2014). However, these estimations have not yet entirely described the whole dehydration range of sepiolite or the mineral reactions involved in geological processes within the Earth's crust. The scarcity of data on sepiolite stability and mineral transformations can be approached from a thermodynamic perspective.

Thermodynamic models constrained by experimental data are used in this study to assess the extent of sepiolite contributions to fault mechanics and earthquake nucleation. The refined model is applied to the natural case of the Galera Fault, which has a sepiolite-rich fault gouge produced by hydrothermal alteration of Mg-rich fluids during periods of fluid-rock interactions that concentrated on fault planes and fractures of the deformation area. XRD data limitations in determining the accurate percentage of sepiolite in the rock are mitigated by performing a thermogravimetric analysis of the fault rock that can confirm sepiolite is the major constituent of the gouge and an optimum candidate to assess the water release, volume changes and mineral reactions that can take place on Galera Fault's active fault planes during ongoing deformation. Previous experimental work on the mechanical properties of the Galera fault gouge showed the strength of the sepiolite-rich gouge to have friction coefficients around 0.47 under water-saturated conditions (Sánchez-Roa et al., 2016). To assess the changes on fault strength in the Galera Fault with changing pressure and temperature, we compare the experimentally-measured friction coefficient of the sepiolite-rich gouge with experimental strength measurements of the friction coefficient of a synthetic gouge mixture based on the mineral assemblage and proportions predicted by the newly proposed thermodynamic model.

This study presents the integration of a new thermodynamic model for sepiolite with frictional tests assessing fault strength, and the application of these methods to a natural example as a strategy to explore the relation between sepiolite dehydration and earthquake nucleation in the Galera Fault Zone.

2. Thermodynamic model

2.1. Considered range of hydration states

Synchrotron XRD data show that the volume vs temperature dehydration curve of sepiolite is a step function (Post et al., 2007), similar to that observed for smectite dehydration. In smectite, this step dehydration results from two different processes: i) continuous loss of interlayer water and constant decrease of volume for a fixed number of water layers, and ii) discontinuous loss of water layers and large volume changes associated with the collapse of the interlayer space at fixed temperatures (see Vidal and Dubacq, 2009 and references therein). Similarly, the step dehydration in sepiolite results from the progressive loss of interlayer water (zeolitic water), as well as the folding of the sepiolite structure that can be compared to the collapse of the interlayer space for smectites. Five end-members with different hydration states (including zeolitic and bound water molecules) and four solid solutions between these end-members must be defined to cover the entire range of possible sepiolite hydration from 12 to 0 H_2O p.f.u: Sepiolite-$12H_2O$, Sepiolite-$6H_2O$, Sepiolite-$4H_2O$, Sepiolite-$2H_2O$, and Sepiolite-$0H_2O$ (Fig. 1). However, given the lack of thermodynamic stability of the experimentally achieved sepiolite-$2H_2O$ and the sepiolite-$0H_2O$, as well as their absence in nature, we restricted our study and thermodynamic model to the "zeolitic water". Following the approach proposed for smectite by Vidal and Dubacq (2009), the step dehydration of sepiolite was modelled with two solid solutions between the zeolitic-water-free end-member Sepiolite-$4H_2O$ and the end-members Sepiolite-$12H_2O$ or Sepiolite-$6H_2O$. The Fe-Mg compositional variation in sepiolite was not included in this model due to the few occurrences of Fe-sepiolite and the lack of Fe-Mg exchange in the studied samples. The exchangeable cations within the channels were also excluded from the model assuming that their contributions are negligible compared to the major differences between the three types of water in the structure, thus they are not expected to affect the dehydration temperatures of sepiolite.

2.2. Thermodynamic approach

In view of the strong similarities with smectite, the thermodynamic