QUANTUM CHEMICAL SIMULATIONS OF AQUEOUS ALTERATION PROCESSES OF MAFIC SILICATES IN CARBONACEOUS CHONDRITES.

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Introduction: The degree of aqueous alteration in the parent bodies of carbonaceous chondrites (hereafter CCs) was highly variable as inferred from the study of the different chondrite groups [1-4]. It is widely accepted that the CI, and CM chondrite groups suffered extensive aqueous alteration, like also most members of the CR group [1,5]. Water was available in these materials at early times because the parent bodies of these meteorites accreted enough ice and hydrated minerals between their rock-forming minerals. Parent body aqueous alteration occurred during the first 10 Ma from the consolidation of their parent bodies as inferred from the formation of carbonates [6-7]. Thermal metamorphism and collisional compaction were the sources of heat needed to release this water into the fine-grained matrix cementing these meteorites. At that time pervasive alteration started and compact chondrules and inclusions were progressively altered. Elemental mobilization took place and the primordial chemistry/mineralogy changed. In general mafic silicates were predominantly forming chondrules and also matrix fragments [1-4]. In order to have deeper insights into the aqueous alteration undergone by meteoritic materials we initiated a study focused on the atomistic simulation of these processes by means of quantum chemical calculations to obtain useful atomic-scale information, such as accurate structural and energetic data. As a first step for this aim, we have studied the reaction of the extraction of metal cations of olivinic materials induced by water. To do this, we have modeled both pure-Mg^{2+} and Fe^{2+}-containing olivine surfaces (Mg_2SiO_4 and $Mg_{1.75}Fe_{0.25}SiO_4$, respectively) and we have simulated the reaction of Mg^{2+} and Fe^{2+} extraction considering as reactants the olivinic surfaces with adsorbed water and as products the same surfaces with a metal cation sequestered by water via their full coordination (Fig. 1).

Technical procedure: All these simulations have been carried out using the CRYSTAL09 ab-initio periodic code [8]. This code implements the Hartree−Fock and Kohn−Sham self-consistent field method to solve the electronic Schrödinger equation for periodic systems [9], and it allows to perform geometry optimizations [10], calculation of one-electron properties and simulation vibrational and reflectance spectra of periodic systems [11]. The multielectron wave function is described by linear combination of crystalline orbitals, which in turn are expanded in terms of Gaussian-type orbital basis sets. Calculations for the present work were based on the B3LYP [12] density functional theory (DFT) method using a standard 6-31G(d,p) basis set. Surface models computed by CRYSTAL09 are true 2D systems (i.e., with infinite empty space above and below the surface slab). In this study, slab models of the crystalline (010) olivine surfaces were adopted, since this is the main cleavage crystallographic plane of Mg_2SiO_4 [13]. These surfaces were derived from cutting out the corresponding crystal bulk structures along the [010] direction. The most relevant structural feature of these surfaces is that they present coordinatively unsaturated metal cations at the outermost positions of the surface.

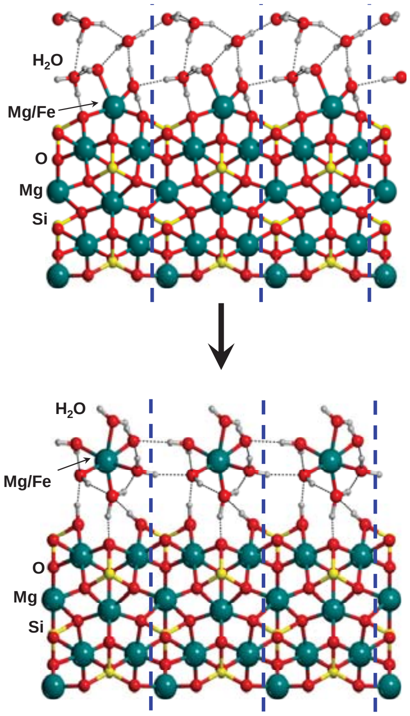

Fig. 1. B3LYP-optimized geometries of the (010) surface models for $(Mg,Fe)SiO_4$ adopted in this work to study the metal cation extraction by action of water. Top-structure: reactant, in which 6 water molecules per unit cell are adsorbed on the surface; bottom-tructure: product, in which the 6 water molecules have extracted the outermost metal cation. Blue dashed-lines indicate the lateral unit cell limits.

Results and discussion: The calculated reaction energies for the process described above, based on pure electronic energies (i.e., calculations at 0 K without including zero-point energy, thermal and entropic corrections), are +20 and +17 kcal mol^{-1} for the extraction of Mg^{2+} and Fe^{2+}, respectively, indicating that the cation extractions are energetically disfavored. The fact that the (010) surfaces are the most stable ones for olivines (and thus, the less chemically active ones) can explain these values. Moreover, these values are limited to electronic energies so the inclusion of thermal and entropic corrections can modify them (work in progress). Nonetheless, it is worth to remark that these values point out that extraction of Fe^{2+} is less difficult than Mg^{2+}, in line with the fact that iron is the major metal that undergone chemical transformations upon aqueous alteration. Moreover, during the geometry optimizations of the product structures, spontaneous proton transfers from the water molecules to oxygen surface atoms, hence forming both metal hydroxides and surface SiOH groups, took place, which is in agreement with the first steps for the serpentinization of olivines according to $4(Mg,Fe)SiO_4 + 6H_2O \rightarrow (Mg_3,Fe_3)Si_4O_{10}(OH)_8 + Mg(OH)_2 + Fe(OH)_2$.

It is known that aqueous alteration observed in CCs had often a “static” nature [14-15], but some evidence of liquid flow has been found [16, 4]. As consequence of hydration some elements were mobilized from the chondrules and inclusions and produced a large variety of mineral phases. As consequence sulfides, carbonates, oxides, etc., precipitated into the matrix (see Fig. 2). We wish to gain insight in these processes to better understand the spatial and temporal scales of these processes. Other interesting issue goes the other way around: if primordial mafic silicates were more magnesian, can parent body mild metamorphism and aqueous alteration make them more ferrosian? [1].

Conclusions: We have initiated a study focused on the atomistic simulation of aqueous alteration processes by means of quantum chemical calculations. Basic models of the crystalline structure of mafic silicates are used together with interacting water in order to derive useful atomic-scale information, such as structural details of the considered materials and reaction energies. The calculated reaction energies point out that extraction of Fe^{2+} is less difficult than Mg^{2+}, in line with the fact that iron is the major metal that undergone chemical transformations upon aqueous alteration. Current available evidence on aqueous alteration in CCs also indicates that Fe is easily mobilized from chondrules, or troilite and metal grains. This element together with S and the alkalis (Na and K) are easily precipitating into the matrix surrounding chondrules and inclusions in order to create secondary minerals that, once dated [7], are the best available evidence of post-accretional parent body aqueous alteration.

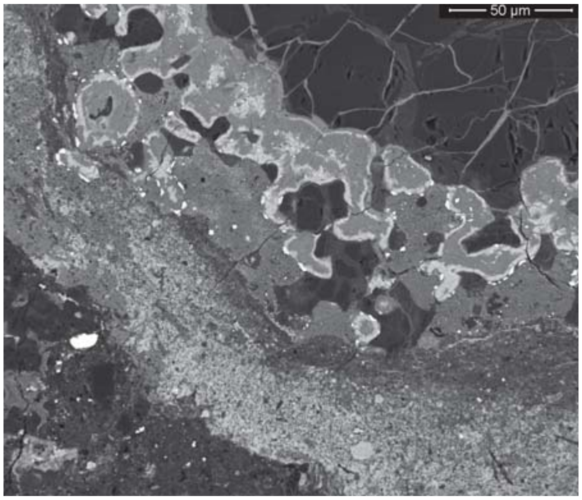

Fig. 2. A Fe- and S-rich rim formed by the aqueous alteration of the mafic silicates forming the glassy mesostases of the right-hand chondrule in CR2 Antarctic chondrite LAP02342.

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