

## Shear deformation of olivine at high pressures and temperatures: An atomic scale perspective

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Olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$ , is assumed to be the most abundant mineral of the Earth's upper mantle. The knowledge of its physical properties in the relevant range of pressures and temperatures therefore provides important constraints on the dynamic behavior of the upper mantle. Plastic deformation of olivine has been investigated for a long time but recent experimental [1] and computational [2] studies suggest a pressure and strain rate dependence of the dominant olivine dislocation slip system from [100] slip at low pressures and low strain rates to [001] at high pressure and high strain rates.

Here, an atomic scale modeling approach is used to investigate the pressure and temperature dependence of the shear deformation mechanism of the magnesium end member,  $\text{Mg}_2\text{SiO}_4$  forsterite. The simulations combine classical molecular dynamics with metadynamics using the scaled simulation cell box matrix as dynamic variables [3]. The particle interactions are described by an advanced polarizable ion potential [4]. Pressure was varied between atmospheric and 20 GPa, temperature between 1000 K and 2000 K. At high pressures ( $> 5$  GPa), the dominant shear is observed in [001], which is consistent with the experimental studies. The dominant shear plane changes from (100) to (010) with increasing pressure and temperature. At lower pressures ( $< 5$  GPa), both shear in [100] and combined shear in [001] and [100] are observed.

Besides identification of shear plane and direction, insight into the atomic scale mechanism of shear is obtained. The most interesting observation is a change of shear mechanism in [001](010) from a two-step process at lower pressure, in which  $\text{SiO}_4$  tetrahedra remain intact and the stacking order of oxygens unchanged, to a three-step process, which involves breakage of Si-O bonds and changes in the stacking order of the oxygen sublattice. The latter mechanism is observed at the highest pressure, where the free volume needed for the other shear mechanism becomes energetically too expensive. Finally, possible relations between shear deformation and high pressure phase transitions of single crystal forsterite will be discussed.

The shear deformation observed in these simulations does not describe the process of dislocation creep but it provides useful guidelines and insights that are not available otherwise. The method used in this study may therefore complement other efforts to understand the rheological behavior of mantle minerals, including the very promising multiscale simulation method presented very recently [5].

[1] e.g. Mainprice et al. (2005) *Science* **433**, 731-733; Raterron et al. (2007) *Am. Mineral.* **92**, 1436-1445; Demouchy et al. (2009) *Geophys. Res. Lett.* **36**, L04304; Hilairet et al. (2012) *J. Geophys. Res.* **117**, B01203. [2] Durinck et al. (2005) *Phys. Chem. Minerals* **32**, 646-654; Durinck et al. (2007) *Eur. J. Mineral.* **19**, 631-639. [3] Martonak et al. (2003) *Phys. Rev. Lett.* **90**, 075503. [4] Jahn and Madden (2007) *Phys. Earth Planet. Int.* **162**, 129-139. [5] Cordier et al. (2012) *Nature* **481**, 177-180.

## Mineralogical controls on arsenic bioaccessibility in mine waste and body fluids

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Arsenic associated with ores is typically hosted in arsenopyrite and/or arsenical pyrite. In mine waste, arsenic mineralogy is much more complicated as a result of weathering, ore processing and the ability of As to be incorporated as As(V), As(III) or reduced As in a wide range of secondary minerals. Gastric to intestinal extraction tests indicate decreasing As bioaccessibility from Ca Fe arsenate > lead arsenate > arsenic trioxide > amorphous iron arsenate > As-bearing Fe oxyhydroxide > arsenical pyrite > As sulfide (realgar) > arsenopyrite. There are likely to be additional factors affecting As uptake in the gastro-intestinal system including changes in pH, redox conditions and availability of Fe and S to combine with dissolved As.

Field and laboratory observations of the stability of As secondary minerals in mine waste may provide insight into the anticipated complexities and As phase transformations in the gastro-intestinal system. Arsenopyrite ( $\text{FeAsS}$ ) is typically coarse-grained relative to secondary minerals, explaining why it does not react during bioaccessibility tests which involve exposure to gastric fluids for only an hour or so. Scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) forms as an oxidation product of arsenopyrite ( $\text{Fe/As} = 1$  for both minerals) and is stable in low pH environments which explains why it releases little As to acid gastric fluids, even when the starting solid is nanocrystalline [1]. As pH increases, scorodite is transformed to hydrous ferric arsenate ( $\text{Fe/As} > 1$ ), which may explain why more As is released to circum-neutral pH intestinal fluids. Tooeleite ( $\text{Fe}_6(\text{AsO}_3)_4(\text{SO}_4)(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ ) has been recognized only rarely in mine waste but precipitates readily when As(III) is combined with Fe(III) under acid conditions ( $\text{pH} < 4$ ) [2] suggesting that if sufficient Fe is available ( $\text{Fe/As} = .66$ ), this phase may form under gastric conditions and limit As bioaccessibility. Arsenic trioxide ( $\text{As}_2\text{O}_3$ ) is a product of ore processing which is stable over a wide range of pH and, in some contaminated soils, persists for many decades. In other situations, arsenic trioxide combines with Fe(III) to form scorodite in acid drainage [3] or with reduced S to form secondary As sulfides [4]. It is possible that similar transformations may occur in the body, both of which would reduce As bioaccessibility. Finally, Ca-Fe arsenate minerals (e.g. yukonite  $\text{Ca}_7\text{Fe}_{12}(\text{AsO}_4)_{10}(\text{OH})_2 \cdot 0.15\text{H}_2\text{O}$ ) have  $\text{Fe/As} > 1$  form under pH-neutral conditions where carbonate minerals are stable. These minerals are soluble in acid fluids and exhibit high As bioaccessibility in gastric solutions.

Laboratory results indicate that As bioaccessibility can actually be higher per mass in simulated lung fluids than gastric, but the overall dose is smaller due to the lower amounts that reach the lung.

[1] Meunier et al. (2010) *Environ. Sci. Tech.* **44**, 2667-2674.

[2] Opio et al. (2011) *Proc. 2<sup>nd</sup> Environmine Sem.* [3] Haffert & Craw (2007) *App. Geochem.* **23**, 1467-1483. [4] Fawcett & Jamieson (2011) *Chem. Geol.* **283**, 109-118.