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SILICA – THE MOST PRIMITIVE MINERAL ON EARTH AND MARS?

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The two kinds of atoms Si and O make up about 75 wt. % of the Earth's crust. Of course, they form the basis of all silicate minerals, but they also occur as pure SiO_2 in many modifications, going from stable α-quartz to high-T phases like tridymite and cristobalite, and to high-P phases, the most extreme one being seifertite, that is expected to be stable at pressures > 120 GPa. At the surface of the Earth the geosphere touches the hydrosphere, so that Si, O and H are the most common types of atoms. Together they form silica (SiO_2 x nH_2O), that might have some kind of atomic long-distance order (like opal-CT) or none (like opal-A). This last type, amorphous silica, is arguably the most primitive mineral substance at the Earth's surface and is in the center of this presentation. In the following three terrestrial occurences are presented, i.e., (1) certain kinds of opal-A from the opal fields of Andamooka/AUS and Yowah/AUS (LIESEGANG et al., 2014); (2) opal-A pseudomorphs after bivalve shells from Coober Pedy/AUS (LIESEGANG et al., 2017); (3) silica crusts on thrown-away beer bottles from Australian opal fields (MILKE et al., in prep.). Silica is also known to be present on the surface of Mars as we know from remote sensing and rovers. Therefore, silica phases in shocked martian meteorites might be derived from amorphous silica, and are the final topic (4) addressed here.

(1) The vast majority of what is called "precious opal" on the world market comes from opal fields in the Great Artesian Basin of Australia. Opal-A from there largely consists of silica spheres with an average diameter of 140-320 nm. LIESEGANG et al. (2014) suggested a quantifiable system for distinguishing between monodisperse and polydisperse silica by the relative standard deviation of sphere diameters, where a clear dichotomy is present. They pointed to various mineral inclusions that make bulk analyses a worthless effort for interpret-tations of silica composition. The mineral combination in the host rock of the Andamooka opal ("Bulldog shale") is dominated by kaolinite and alunite, which points to opal formation near pH 3, very close to the isoelectric point of the silica-water system, i.e. the most stable physicochemical region for an aqueous silica colloid (ILER, 1979).

(2) Perfectly fossilized cretaceous bivalve shell fossils consisting of amorphous silica have been analyzed using focused-ion-beam (FIB) and scanning electron microscopy (SEM) methods (LIESEGANG et al., 2017). Some, but not all of those opalized fossils, comprise well-stacked monodisperse silica spheres. Their symmetry is near to closest packed spheres with lattice plane distances in 100s of nanometers, thus despite being

X-ray amorphous they are photonic crystals. The amorphous silica spheres replicate three features of the precursor calcite crystals as is shown by their respective angles: (i) twin lamellae; (ii) cleavage planes; (iii) {104} lattice planes (rhombohedral faces). This observation is explained by a mechanism called interface-coupled dissolution-polymerization-precipitation that evolves via aggregation of silica nanoparticles.

(3) Glass objects (most of them in fact beer bottles) are dug up in the Australian opal fields since the recent miners work in the same areas as their predecessors with ever heavier ma-chinery. The glass usually was buried in the soil for a couple of decades. In places, it displays a play of colour like “precious opal”, and superstition among opal miners makes these sites promising for big finds. The coloration phenomenon comes from a layer structure of amor-phous silica that forms by weathering on the glass surface, following an interface-coupled dis-solution-precipitation mechanism. The layering is surprisingly regular for each sample, vary-ing respectively in the 200-400 nm scale. Such layers therefore are 2D Bragg reflectors. Al-though the interference of light leads to analogous phenomena, the mechanism of formation is completely different from natural opal. It is explained by an interplay between the movement of the glass-silica replacement front and the dehydration/polymerization within the silica pre-cipitate. Since both processes occur linear in time under constant weathering conditions, the result is a regular 2D layer grating.

(4) Seifertite was found as a mineral in a martian Meteorite (SHARP, 1999). This extreme-HP modification of silica is thought to be stable at P > 120 GPa, but recent experiments showed that it can form metastably at much lower pressure (KUBO et al., 2015). This finding is important for the size estimation of impact events on Mars. Pure SiO_2 in shocked martian meteorites might have evolved from high-T modifications present in precursor rocks or the degradation of other silicate minerals. However, it might also have formed from amorphous silica that is present on the surface of Mars. It is hypothesized that hydrous amorphous silica might provide the easiest transition to seifertite during shock metamorphism, as it is the most unstable form of silica at extremely high P-T. Experiments are currently under way.

Being the most primitive mineral substance at the surface of the Earth, silica displays more degrees of freedom than other materials, which might be the reason for its stunning self-organization.

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