SILICA CRACK PATTERN RESEMBLING BALLEN FORMED IN A CIRCULATING FLUIDIZED BED BOILER: IS SHOCK NECESSARY TO FORM BALLEN?

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Introduction: The term ballen silica as a purely descriptive definition refers to clusters of curved cracks in quartz or cristobalite, which are commonly observed in shocked rocks from terrestrial impact structures [1]. However, the occurrence of ballen silica as possible microscopic evidence of shock has been debated [2]. The ballen microstructure has been supposed to form by devitrification of either silica glass [1] or lechatelierite [3]. Locally, ballen silica has been reported in association with the shock-induced high-pressure polymorph of silica coesite and with planar deformation features in quartz [1,4]. Here we present crack patterns resembling ballen silica in the slag that formed in the combustion chamber of a biomass power plant in Vienna (Austria), fueled with wooden chips and employing a fluidized bed of quartzose sand for heat transfer. The synthetic crack pattern and natural ballen silica in samples from the Bosumtwi and the Ries impact structures (described in [2]) have been analyzed by Raman spectroscopy. Atmospheric pressure conditions and the moderate temperatures reached in the biomass combustion chamber allow a new discussion of ballen microstructure formation.

Methods: A polished thin section (35 µm thick) of the slag was prepared for petrographic investigations. After preliminary optical microscopy, Raman spectroscopy was performed with a Horiba Jobin Yvon LabRAM HR Evolution confocal Micro-Raman spectrometer, with a 632.8 nm (red) emission of a He–Ne laser for excitation, 1800 grooves/mm grating and a resulting spectral resolution <1 cm^{-1}. Spectra were collected by accumulation of twice 60s acquisition time. The circulating fluidized bed boiler was fed with natural wood having an average composition of 50% C, 44% O, and 6% H, with trace amounts of N, S, and Cl. The bed consists of 98% quartz sand, with minor contents of Al_2O_3 and Fe_2O_3 and an average grain size of 0.7 mm. The process temperature in the combustion chamber supposedly did not exceed 1000°C (A. Pesek 2017, personal communication). For technical information on the power plant and a preliminary characterization of the slag refer to [5].

Results: The slag consists of a whitish agglomerate of silica particles in a glassy matrix, with local relics of wood. The silica particles consist of angular quartz fragments surrounded by cristobalite. The characteristic curved cracks, closely resembling the so-called ballen silica, are localized in cristobalite. In contact with the glass matrix, fine-grained euhedral or subhedral cristobalite crystals were observed. Ballen cracks occur in both quartz and cristobalite in the natural samples and locally the two phases coexist, as shown in [2].

Discussion and conclusions: Cristobalite is common in volcanic rocks, resulting from either precipitation from silica vapor or devitrification of silica glass [6-7]. In volcanic rocks, the formation of curved cracks, referred to as fish-scale microstructure, is generally associated with the β- to α-cristobalite phase transition during cooling below 270°C [8-9]. The non-shock origin of ballen silica has already been discussed in the literature, [10] proposed devitrification of a silica-saturated melt, similarly to volcanic rocks, and [11] suggested brittle fracturing of quartz due to shock thermal gradient, excluding the transition of the material through amorphous or melt phases. In the slag material, cristobalite likely formed by both solid-state transformation of quartz (within the silica particle) and by crystallization from the melt (at the rim of the particle, in contact with the glass matrix). Minor component impurities (such as Al_2O_3 and Na_2O) and crystal defects have possibly lowered the temperature of cristobalite formation with respect to theoretical predictions based on equilibrium thermodynamics in the pure SiO_2 system [6;12-13]. In natural and synthetic samples, curved cracks forming ballen microstructures are supposed to have formed during the transition of β- to α-phase of both quartz and cristobalite during cooling, which implies >5% volume reduction for both phases. Further investigations are expected to clarify whether the nucleation of cracks might be related to local impurities or grain boundaries and to characterize their 3-D geometry. In conclusion, unless associated with high-pressure silica polymorphs (as discussed in [2]) or with other unique shock indicators, the occurrence of ballen silica alone cannot prove an impact event.

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