The size dependent interaction between nanoparticles and collagen: Implications for biomineralization

DONGBO WANG[1(*)], JING YE[1], STEVEN HUDSON[1], VIVEK PRAHBU[1], KEANA SCOTT[2] AND SHENG LIN-GIBSON[1]

[1]Polymers Division, National Institute of Standards and Technology, dongbo.wang@nist.gov (* presenting author)

[2]Surface and Microanalysis Division, National Institute of Standards and Technology

Collagen is the primary structural protein found in connective tissues, making up more than 25 % of the whole-body protein content. It is also the primary biological molecule responsible for the organization of mineralized tissue. Bone and teeth are surprisingly complex organic/inorganic hybrid structures mainly composed of type I collagen and the calcium phosphate mineral – hydroxyapatite (HA). These tissues are hierarchically organized from the nanometer to the meter length scales. Traditionally, collagen mineralization was thought to occur by calcium phosphate nucleation and growth processes from dissolved ions. Recently, these ideas have been challenged and the new concept of "non-classical" mineralization has emerged[1]. In biological tissues it is now proposed that the mineralization process starts with the formation of small amorphous calcium phosphate (ACP) clusters, which infiltrate collagen, and then transform to form intrafibular HA.

We begin to test this new "non-classical" understanding of collagen mineralization by studying the interaction between collagen matrices and colloidally stable/non-reactive gold nanoparticles as models for ACP. We measure *in situ* changes in collagen matrix mechanical properties after introduction of gold nanoparticles using Quartz Crystal Microbalance with Dissipation monitoring (QCM-D). The QCM-D data show a particle size dependent interaction, where 2 nm particles strongly interact with the collagen matrix and cause stiffening in the bulk. Larger particles (3 nm – 40 nm) only interact to the surface of the collagen matrix and don't penetrate into the bulk. We observe the same interaction dynamics with both positively and negatively charged nanoparticles. These results have been confirmed through imaging by AFM and FIB/STEM. However, 2 nm particles, which are comparable in dimension to ACP clusters may not fully infiltrate into collagen fibrils. Therefore size alone likely does not fully explain the ability of ACP clusters penetrate into collagen and form mineralized structures. Continuing work focuses on using QCM-D to investigate stabilized calcium phosphate nanoparticles and their interactions with collagen matrices.

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Geochronology and tectonic nature of "Precambrian" basement in eastern Heilongjiang province, NE China: constraints from zircon U-Pb dating

F. WANG[1], F.H.GAO[1*], W.L. XU[1], W.L. HAO[1], H.H. CAO[1]

[1]College of Earth Sciences, Jilin University, Changchun 130061, China (jlu-wangfeng@sohu.com, *gaofuhong213@sina.com)

NE China is located in the eastern section of the Central Asian Orogenic Belt (CAOB) [1]. The region includes the Erguna, Xing'an, Songnen-Zhanguangcai Range, and Jiamusi massifs from west to east. Recently, with application of modern dating techniques, previously beleived Precambrian strata in the Erguna, Xing'an, and Jiamusi massifs have been almost disintegrated into sedimentary and igneous rocks with different Paleozoic ages rather than Precambrian [2-4]. Then, when did the previously determined Precambrian strata including the Dongfengshan (DG), Zhangguangcailing (ZG), and Yimianpo groups (YG) in the Songnen-Zhangguangcai Range Massif form? These Precambrian strata are composed of a set of meta-sedimentary and volcanic rocks. The dating results, together with field geology, indicate that the oldest sedimentary unit from the DG deposited later than 821 Ma, whereas the youngest sedimentary unit deposited during Early Permian (275~271 Ma), that the sedimentary rocks from the YG formed later than Late Triassic (223 Ma), whereas the volcanic rocks from the YG formed in Early Jurassic (179~189 Ma) and Early Permian (271~292 Ma), respectively, and that the oldest sedimentary rocks from the ZG formed during 450~426 Ma, whereas youngest sedimentary rocks formed during 226~211 Ma. The above dating data indicate that the ZG and YG formed from Early Paleozoic to Early Mesozoic, whereas the majority of the DG formed from Early to Late Paleozoic, some of them formed in the Neoproterozoic. Combined with field profile and dating results, we conclude that the ZG could be a tectonic mélange and the melanging could take place during Early-Middle Jurassic.

Furthermore, sediment provenance analysis indicates that nearly all the sediments of these previously beleived Precambrian strata directly sourced from the Phanerozoic intrusions in the Songnen-Zhangguangcai Range and Jiamusi massifs while widespread occurrence of the detrital zircons with ages of 0.8~0.9 Ga and 1.8 Ga as well as 2.4-2.5 Ga implies the existences of the Neoproterozoic magmatisms and remnants of an ancient Precambrian basement within the Songnen-Zhangguangcai Range Massif in eastern Heilongjiang Province, NE China.

This research was financially supported by research grants from the Natural Science Foundation of China (Grant 41072038).

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