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Characterization and ^{10}Be content of iron carbonate concretions for genetic aspects – Weathering, desert varnish or burning: Rim effects in iron carbonate concretions

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ABSTRACT

The research investigated three iron carbonate (siderite) sedimentary concretions from Nagykovácsi, Úri and Délegyháza, Hungary. To identify possible source rocks and effects of the glaze-like exposed surface of the concretions, we carried on comparative petrological, mineralogical, geochemical and isotopic studies. The samples were microbially mediated siderite concretions with embedded metamorphous and igneous mineral clasts, and had specific rim belts characterized by semi-concentric outer Fe-oxide layers, fluffy pyrite-rich outer belts and siderite inner parts. We investigated the cross section of the Fe-carbonate concretions by independent methodologies in order to identify their rim effects. Their superficial oxide layers showed evidence of degassing of the exposed surface caused most probably by elevated temperatures. The inner rim pyrite belt in the concretions excluded the possibility of a prolonged wet surface environment. Microtextural and mineralogical features did not support desert varnish formation. ^{10}Be nuclide values of the Nagykovácsi and Uri concretions were far above the level of terrestrial in-situ cosmogenic nuclides, but they were consistent with the lowest levels for meteorites. Though the data were not conclusive to confirm any kind of known origin, they are contradictary, and open possibilities for a scenario of terrestrial meteorite origin.

1. Introduction

1.1. Terrestrial radiogenic nuclides

Rocks exposed on the Earth's surface suffer changes, which

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cause transformations of the exposed surface such as microtexture, mineralogy, chemistry and isotopic composition, resulting formation of an outer rim. We overview all these changes in a multi-hierarchical comparative analyses in order to distinguish three different ways of transformations: weathering, desert varnish formation or burning at highly elevated temperature. In order to strengthen the distinction by the exposition time, we also determined ^{10}Be and ^{14}C contents. Among commonly measured long lived terrestrial cosmogenic isotopes, ^{10}Be is routinely used in geological and geomorphological investigations, as well as in meteorite research. The primary cosmic rays generate secondary radiation, which results numerous so called terrestrial cosmogenic radiogenic nuclides in the atmosphere and in the rocks and sediments exposed at the surface of the Earth (lithosphere) via nuclear reactions such as ^{3}He, ^{14}C, ^{39}Ar, ^{36}Cl, ^{26}Al, ^{10}Be, ^{32}Si, ^{21}Ne, ^{41}Ca (Wagner, 1998). The half-life of ^{10}Be is 1,387,000 yr (Chmeleff et al., 2010; Korschinek et al., 2010) and it is used for exposure dating of rocks, soils, ice cores and also for meteorites. Concentration in cosmogenic nuclides in minerals depends among other things on exposure time, latitude, altitude, topography, type of mineral, organic matter content and type of cosmogenic nuclide.

1.2. Desert varnish

Fourteen different types of coatings cover rock surfaces in every terrestrial weathering environment, altering the appearance of the underlying landform (Dorn, 2013). Rock varnish (often called "desert varnish") is a paper-thin mixture of about two-thirds clay minerals cemented to the host rock by typically one-fifth manganese and iron oxyhydroxides. Upon examination with secondary and backscattered electron microscopy, the accretionary nature of rock varnish becomes obvious, as does its basic layered texture imposed by clay minerals (Dorn, 2008). The major elements are O, H, Si, Al, and Fe in approximately equal abundance with Mn. Varnish Mn:Fe ratios vary from less than 1:1 to over 50:1, in contrast with Mn:Fe ratios of about 1:60 in the Earth's crust. Concentrations of over 80% Mn in focused spots occur on budding bacteria forms (Dorn, 1998). Varnish minerals are amorphous (Engel and Sharp, 1958), with goethite (Scheffer et al., 1963) and ferric chamosite (Washburn, 1969) as important components. Seminal research conducted with infrared spectroscopy, X-ray diffraction and electron microscopy revealed that the bulk of rock varnish is composed of clay minerals (Potter and Rossman, 1979), dominantly illite, montmorillonite, and mixed-layer illite-montmorillonite. As previously noted, the layering seen in varnish at all scales reflects this clay mineralogy. Subsequent research has confirmed the dominance of clay minerals (Dorn, 1998, 2008; Krinsley, 1998; Dorn and Krinsley, 2011).

1.3. Siderite

There were two iron-carbonate (siderite, $FeCO_3$) concretions of exotic outlook, Nagykovácsi (Nk) and Úri, and also sedimentary siderite concretions and fragments as counterparts from Délegyháza, Hungary, that may be the probable origin of the concretions.

On the chance that these samples represent "meteorites" on the surface, the possible existence of which is raised in the literature (Melosh and Tonks, 1993; Simms, 2011), siderite looks to be the best candidate. Via atmospheric heating, magmatic and metamorphic rocks get a melted fusion crust which is very similar to silicate meteorites. Among sedimentary rocks, the most common are carbonates (limestone, dolomite), claystones and sandstone, the last too are often soft. Limestone ($CaCO_3$) and dolomite [$(CaMgCO_3)_2$] suffer degassing of the exposed surface on heating, similarly to siderite, but its color indicates a need for macroscopic attention (shiny brown appearance), and the carbon isotopic and mineralogical changes can prove degassing. The macroscopic features of limestone and dolomite do not differ much from the original rock after degassing causing difficulties in identification of their origin and recognition on the surface.

Among the aims of our study was whether the routinely used methodologies can distinguish siderite objects with various origin from each other convincingly, or not. Further, whether can we distinguish the rim effects on the exposed surfaces of the concretions convincingly according to formation processes including weathering, desert varnish coating formation, or burning (degassing) at highly elevated temperatures. Last but not least, we provide high resolution data on exposed surfaces (surface and boundary transitional zones) of siderite samples, which are scarce in the literature.

2. Samples and methods

2.1. Samples

The *Nagykovácsi (Nk)* sample was collected at Nagykovácsi village, the Úri sample at Úri village (Fig. 1). The motivation of sampling was the exotic occurrence of the samples. The Nk showed a pale, shiny, brownish-grayish color (Fig. 2A). Its ellipsoidal shape was 3.8 cm × 3.4 cm x 2.6 cm in size. Its mass was 66.7 g.

The Úri sample was very similar to Nk, characterized also by pale brownish-grayish color. Its ellipsoidal shape was 5.2 cm × 3.2 cm x 2.8 cm in size. Its mass was 79.9 g. The samples were covered by small thumbprint-like indentations (resembling to regmaglypts). Basic data and the methods used on the samples are summarized in Table 1 and Fig. 2.

Danube pebble (DH) samples were collected in pebble queries near the river Danube, where they are common constituents in the sediments of the ancient Danube (*Délegyháza*, Fig. 1). They are of indeterminate shape with variable sizes from a few cm to some tens cm (Fig. 2A). In some regions it is covered by small thumbprint indentations (resembling to regmaglypts), and partially covered by dark-yellow brown rims. Its fine-grained matrix with embedded mineral clasts was very similar to Nk and Úri (Supporting Information hereafter SI. 1–3).

The samples had a shiny glaze-like cover consisting of Fe-oxide, which defends inner parts of the samples from transitional, among them weathering processes (e.g. pyrite and siderite).

2.2. Methods

Mineral composition was identified by X-ray powder diffraction (XRD) at Eötvös University Dept. Mineralogy, Budapest (Philips diffractometer (PW 1710) with carbon monochromator and Cu Kα radiation), and at Institute for Geological and Geochemical Research, Budapest. Mineral composition was determined on randomly oriented powdered samples by semi-quantitative phase analysis according to the modified method of Bárdossy et al. (1980), using previously defined intensity factors.

^{57}Fe Mössbauer spectra of powered subsamples (Nk-4ab, Nk-3ab-D, Nk-3ab-T) were recorded by conventional Mössbauer spectrometers (WISSEL and HAS Institute for Technical Physics and Material Sciences, Budapest) working in constant acceleration mode in transmission geometry at 293 K and between 20 K and 200 K. A closed circuit refrigerator based cryostat (APD) was used for the low temperature measurements. A 50 mCi activity ^{57}Co(Rh) source supplied the gamma rays for the measurements. The isomer shifts were given relatively to α-Fe. The evaluation of the Mössbauer spectra were carried out via the least squares fitting of

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