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Isotope wallrock alteration associated with hypogene karst of the Crimean Piedmont, Ukraine

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ABSTRACT

Although it is commonly perceived that isotopic alteration of carbonate rock is suppressed at low temperatures (below ca. 80–100 °C), this study demonstrates that alteration halos do develop in permeable limestones of relatively low textural maturity. The study of Paleogene carbonate bedrock constituting the walls of hypogene karst conduits of the Crimean Piedmont (Ukraine) revealed several events of water–rock interaction, each resulting in isotopic alteration of the bedrock.

Early development of hypogene karst conduits shifted $\delta^{18}O$ and $\delta^{13}C$ toward lower values by 1–2‰ and 1–3‰, respectively. The width of the alteration zone locally exceeds several meters. The case hardening associated with cavernous weathering shifted $\delta^{18}O$ and $\delta^{13}C$ of the bedrock toward slightly more positive values (by up to 3‰ and 1‰, respectively). The thickness of isotopic halos ranges from a few centimeters to tens of centimeters. During late-stage hypogene karstification the $\delta^{18}O$ values of the bedrock was shifted toward lower values (by 5–6‰), forming a thin (5–15 mm) alteration halo. In most cases $\delta^{13}C$ was also shifted toward lower values (by 6–9‰), but in one case a shift toward higher values (by ca. 2‰) was observed.

Water involved in early hypogene karst and in the origin of cavernous weathering structures was enriched in ^{18}O. Such waters are known in Crimea in association with mud volcanoes on the Kerch Peninsula. We suggest that similar deep-seated water affected the Crimean Piedmont during the Middle Miocene. Water involved in late hypogene karstification had δD values of −75 to −68‰ and $\delta^{18}O$ values of −10 to −9‰ (fluid inclusion data), similar to present-day spring and well water in Crimea. Isotopic calculations and fluid-inclusion data indicate that the late hypogene karst processes occurred at low temperatures (<ca. 50 °C). These processes ceased before 130 ka, when the Crimean Piedmont was uplifted, dissected by erosion, and acquired its modern morphology.
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1. Introduction

1.1. Isotopic alteration of bedrock in karst systems

The term karst (karstification) refers to the processes of water–rock interaction, which results in significant dissolution of the rock and creation of specific solutional morphologies, both on the surface (karst relief) and in the underground (caves). The two primary classes of karst are distinguished. The *hypergene (epigenic) karst* involves gravity-driven water recharged at the overlying or immediately adjacent land surface, whose aggressiveness is derived, primarily, from near-surface sources (typically the soil zone). In *hypogene karst* the water acquires its aggressiveness from deep-seated sources and is recharged from below. Water involved in hypogene karstification commonly, but not always, has elevated temperatures (for more discussion see Klimchouk, 2007; Dublyansky, 2012; Klimchouk, 2012; Dublyansky, 2014).

Our working hypothesis is that besides dissolution of bedrock and precipitation of secondary minerals (speleothems), hypogene karst may give rise to isotopic alteration of the bedrock. Studying such alteration may yield important information regarding the physico-chemical parameters of karst water. This may be particularly important when studying fossil karst, whereby the karst water is no longer available for direct analysis.

For carbonate rocks, changes in the oxygen isotope composition are most informative. This is because the extent of its fractionation between water and carbonate minerals strongly depends on temperature. The equilibrium fractionation factor, expressed as 1000lnα, corresponds to the maximum achievable fractionation between a water and rock at a given temperature. Because alteration may not necessarily achieve full equilibrium, the actual fractionation amount may be smaller.

The application of this approach to hypergene (i.e. ambient-temperature) karst is difficult due to inherent constraints of the system. The isotopic composition of oxygen in typical sedimentary carbonate rocks ($\delta^{18}O_{rock}$ = −4 to 4‰ VPDB or 27 to 35‰ VSMOW) is significantly different from the typical composition of karst water ($\delta^{18}O_{water}$ = −5 to −15‰ VSMOW). At temperatures characteristic

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of hypergene karst, the fractionation factor between water and calcite is large and tends to compensate for this difference. As a result, the magnitude of isotopic alteration of bedrock is small (Fig. 1). In addition, kinetics of water–rock interaction is sluggish at low temperatures and the residence time of water (i.e., time available for water–rock interaction) is commonly short in hypergene karst, which further limits alteration. On top of that, hypergenic karst waters are commonly highly aggressive, and the removal of the material from cave wall by dissolution may outpace the propagation of the alteration front into the rock.

With increasing temperature, e.g., at the conditions of hypogene karst, the fractionation factor diminishes, and the potential effect of water–rock interaction becomes greater (Fig. 1). Elevated temperatures also increase the rate of chemical and isotope exchange reactions. In addition, hypogene processes are typically less dynamic, waters move slowly, and the time available for water–rock interaction is hence longer. Traces of isotopic alteration, therefore, have a higher chance to be present in hypogene karst systems.

Carbonate bedrock may also interact with dissolved inorganic carbon (DIC) present in water, which may result in changes in the isotopic composition of carbon. The isotopic composition of DIC is controlled by the sources of carbon in the solution (i.e., soil, dissolving bedrock, locally also deep-seated sources) and is almost independent of temperature.

Isotopic alteration of the bedrock was studied extensively in hydrothermal systems, particularly in the context of ore-forming processes and the formation of hydrocarbon reservoirs (e.g., Sverjensky, 1981; Ohmoto, 1986). Alteration halos around ore mineralizations up to several kilometers wide were identified by changes in the carbon and oxygen isotopic composition of carbonate host rock (Naito et al., 1995; Kesler et al., 1996; Nesbitt, 1996). The stable isotope composition of such carbonate rocks is used as a diagnostic tool for mineral exploration (Barker et al., 2013). In hypogene karst systems isotopic alteration of bedrock was reported from the Black Hills of South Dakota, USA (Bakalowicz et al., 1987), Movile cave in Romania (Sarbu and Lasku, 1997), Cupp Couttun cave system in Turkmenistan (Bottrell et al., 2001), and several caves in Austria (Dublyansky and Spötl, 2009a; Spötl et al., 2009).

The purposes of this study are threefold: (a) to empirically check if isotope alteration halos can develop in the course of the low-temperature water–rock interaction (i.e. below ca. 80–100 °C) during hypogene karstification, (b) to identify the mechanisms responsible for stable isotope alteration in such conditions, and (c) to reconstruct the physico-chemical, geological, and hydrogeological conditions during the development of the hypogene karst in the Crimean Piedmont.

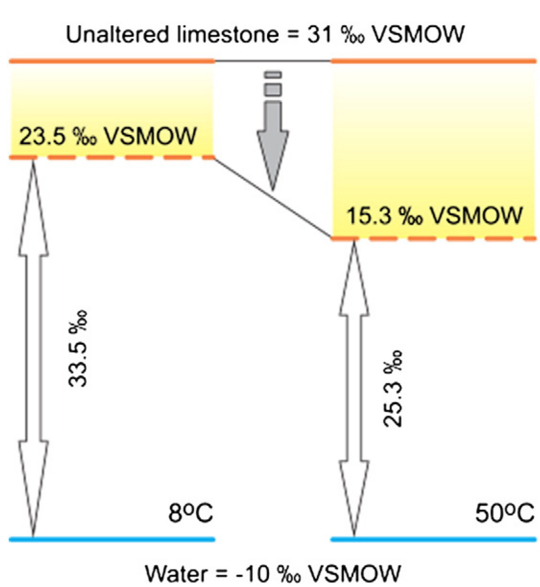

Fig. 1. Equilibrium isotopic alteration effect during alteration of limestone at 8 and 50 °C. White arrows show the equilibrium fractionation factor 1000lnα calculated using the equation of Coplen (2007).

1.2. Hypogene karst in the Piedmont of Crimea

The Crimean Piedmont includes the Inner (the Second) and the Outer (the Third) Ranges of the Crimean Mountains, as well as the inter-range lowlands. It stretches for some 130 km as an arched belt 15–20 km wide from the hills of the Mekenzievy Mountains near the city of Sevastopol in the west to the Agarmish massif near the town of Stariy Crym in the east. The flatland of the North Crimean Plain and the Kerch Peninsula are located to the North and East, respectively.

Structurally, the Inner Range is located at the junction between the fold–thrust structure of the Mountainous Crimea and the Scythian Plate. The first-order element of this zone is the Mesozoic Predgornaya Suture, which formed as a result of the collision of the paleo-terrain of the Mountainous Crimea with Eurasia in Jurassic to Early Cretaceous times (Yudin, 2011). This structural setting is responsible for the enhanced geodynamic activity in the region in the Early Cretaceous, as well as in later times.

The upper structural storey of the Piedmont comprises weakly dislocated, predominantly carbonate rocks of the Upper Cretaceous, Paleogene and Neogene, which form a homocline, dipping ca. 5° to the North. Further to the North, under the northern Crimean Plain, the Cretaceous–Paleogene strata plunge steeply to a depth of 600–1000 m. The south-facing slopes of the Inner Range are typically steep, resulting in a characteristic cuesta relief with cliffs built up of the Paleocene and Eocene limestones.

Until recently, karst was considered only weakly developed in the Inner Range and virtually absent in the Outer Range of the Crimean Piedmont. Rare karstic forms described from the Paleocene and Eocene limestones of the Inner Range included scarce surficial features (subdued karren and sinkholes on the structural surfaces of cuestas) as well as small linear caves. Karstification was thought to have occurred under geomorphological, hydrogeological, and climatic conditions similar to today. Accordingly, recharge was thought to have been restricted to the structural surfaces of cuestas, which are sparsely vegetated and commonly devoid of soil, and groundwater was regarded to flow laterally toward the adjacent depressions. Generally, the geological and climatic conditions were considered not to be favorable for karst. The origin of conspicuous rock shelters, niches, tafoni-like cavities (see Section 4.3) and other sculptural morphologies on the cliffs of the limestone cuestas was attributed to complex denudation included deflation, desquamation, gravity removal and surface wash-out (e.g., Dushevsky, 1987; Dushevsky and Kuznetsov, 1991; Blaga and Popov, 2009).

Comprehensive studies recently carried out by the Ukrainian Institute of Speleology and Karstology led to a fundamentally new understanding of the origin and evolution of karst in the Crimean Piedmont, based on the hypogene karst model (Klimchouk et al., 2009; Amelichev et al., 2011; Klimchouk et al., 2011; Klimchouk and Timokhina, 2011; Timokhina et al., 2011, 2012; Klimchouk et al., 2013). The model calls for the formation of solutional channels in confined hydrogeological conditions via interaction of deep-seated water ascending along vertical fracture pathways with shallow strata-bound water, moving primarily through porous media. The hypogene origin of these channels is supported by multiple lines of evidence, ranging from characteristic morphologies and speleothems to the reconstruction of the evolving regional geological and hydrogeological conditions (Klimchouk et al., 2013). Importantly, cross-formational hypogenic karst structures are shown to guide the denudational dismembering of the original homocline of the Piedmont and the formation of cuesta cliffs. As a consequence the abundant solutional features in the cliffs are now interpreted as morphologies related to former conduits. These morphologic features occur at different spatial scales, ranging from enterable caves down to localized zones of cavernous weathering.

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