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New C–O isotopic data on supergene minerals from the Skorpion and Rosh Pinah ore deposits (Namibia): Genetic and paleoclimatic constraints

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Skorpion and Rosh Pinah Zn-(Pb) deposits are hosted in Neoproterozoic rocks that are part of a volcano-sedimentary sequence within the Gariep Belt of southwest Namibia. Skorpion is the largest Zn-nonsulphide mineralization ever discovered. It formed from weathering and oxidation of a volcanic hosted massive sulphide (VMS) protore and mostly consists of Zn-oxidized minerals. Rosh Pinah is a hybrid Zn massive sulphide deposit, with some VMS and Broken Hill-type characteristics and partly weathered in the uppermost part of the massive sulphide lens.

We compared the deep oxidation process that occurred at Skorpion with the limited weathering of the Rosh Pinah deposit by studying the carbon and oxygen isotope ratios of supergene carbonates minerals. Twenty three smithsonite samples from the Skorpion deposit and 6 gossanous samples (containing both host dolomite and smithsonite) from the uppermost levels of the Rosh Pinah mine have been analysed. The Skorpion smithsonites form botryoidal crusts overgrown by euhedral calcite crystals. At Rosh Pinah all sampled smithsonites occur in veins within the dolostone host rock. Skorpion smithsonite is characterized by $\delta^{13}C$ values strongly variable between −9.1‰ and 0.1‰ VPDB and by a small range in $\delta^{18}O$ from 28.0 to 29.9‰ VSMOW. Calcite shows a minor variation in $\delta^{13}C$ with values being generally positive (0–1.6‰ VPDB) and $\delta^{18}O$ values slightly lower than those of smithsonite (25.4–27.1‰ VSMOW). The analyses of the Rosh Pinah samples show that the host dolomite is characterized by $\delta^{18}O$ values ranging from 18.7 to 22.0‰ VSMOW and by negative $\delta^{13}C$ values (−5.9 to −2.7‰ VPDB). The carbon isotope ratios of smithsonite, as in Skorpion, are negative (−2.8 to −1.9‰ VPDB) and partly overlapping with those of the host dolomites. The $\delta^{18}O$ values (26.7–29.0‰ VSMOW) are on average comparable with the values measured at Skorpion. The similar negative $\delta^{13}C$ values of smithsonite and dolomite at Rosh Pinah point to the involvement of both re-oxidized organic carbon and host dolomite inorganic carbon during smithsonite formation, whereas at Skorpion a larger contribution of isotopically light organic carbon is considered more probable. The comparable $\delta^{18}O$ compositions of smithsonite from the two deposits imply similar ore-forming fluids and/or similar temperatures conditions during formation. In agreement with former studies, we suggest that Skorpion smithsonite precipitated at an average temperature near 17 °C from fluids depleted in ^{13}C due to a high contribution of soil organic carbon, either during the first (Late Cretaceous-Paleocene) or the last humid climatic stage (early-middle Miocene). Even if the similarity between the $\delta^{18}O$ composition of Rosh Pinah and Skorpion smithsonites points to similar ore-forming fluids and/or similar conditions during formation, the relatively high $\delta^{13}C$ values of the Rosh Pinah smithsonites suggest a minor influence of isotopically light organic carbon and the absence of soils over this deposit. Combining these data with the limited thickness of the supergene zone over the latter orebody, it is likely that the Rosh Pinah smithsonites, together with the gossan in which they occur, formed at the end of the early-middle Miocene semi-humid period.

The $\delta^{18}O$ and $\delta^{13}C$ compositions of Skorpion calcite indicate that the precipitating supergene fluids remained roughly unchanged, but that the bicarbonate from the host rock became prevailing. This

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suggests that calcite formation occurred at the beginning of the last late Miocene-Pliocene semi-arid period, when the host marbles were uplifted and karstified, thus promoting a higher bicarbonate contribution from dissolving host rock.

1. Introduction

This study focuses on a comparison between the C-O isotopic geochemistry of carbonate minerals precipitated in the oxidation zone of the Rosh Pinah base metals deposit (Gariep Belt, Namibia) and in the Skorpion nonsulphide Zn mineralization located nearby (Borg et al., 2003) (Fig. 1). The Rosh Pinah and Skorpion base metals concentrations together with other smaller occurrences form a major Zn (+Pb and minor Cu) district in southern Africa (Schneider and Walmsley, 2004). The deposits were both subjected to weathering processes that may have started after the end of the pan-African tectonic phase, followed by uplift and denudation and ended with the onset of a strong arid period that began at least in the Oligocene. However, while the mineralization at Skorpion was almost completely transformed into an economically valuable nonsulphide deposit, at Rosh Pinah, the weathered zone has a limited extension and the majority of the primary sulphides have been preserved. Carbon and oxygen isotopes of smithsonite have been measured in order (i) to elucidate the conditions of supergene ore formation and (ii) to identify the sources of the mineralizing fluids. Stable isotopes of calcite have been analysed only in Skorpion. Stable isotope data on Skorpion smithsonites were previously published by Borg et al. (2003) and Kärner (2006), but no data currently exist for the Zn carbonates occurring in the oxidation zone of the Rosh Pinah mine. In this study, we integrate the stable isotope data sets of the Skorpion carbonates and fill the existing gap regarding the carbonate minerals of the supergene zone at Rosh Pinah. The results also add to the interpretation of the post-Gondwanan paleoclimatic evolution in the Gariep Belt.

2. Geological setting

2.1. Regional geological setting

The Late Proterozoic Gariep Belt (Fig. 1) is regarded as the southern extension of the Damara orogenic front of central and northern Namibia (Davies and Coward, 1982; Reid et al., 1991; Stanistreet et al., 1991; Gresse, 1994; Frimmel, 2000; Jasper et al., 2000; Frimmel et al., 2002). It is subdivided into an eastern para-autochthonous zone, the so-called Port Nolloth Zone (PNZ), and a western allochthonous zone, the Marmora Terrane. The PNZ evolved from an intracontinental rift to a passive continental margin on the western edge of the Kalahari Craton (Jasper et al., 2000). Regional stratigraphic correlations of the Late Proterozoic rock sequence within the Gariep Belt have been subject of considerable debate and several stratigraphic schemes have been proposed by different authors (e.g. Alchin et al., 2005 and references therein). This is a result of poor, isolated outcrops, complexly deformed rock sequences and rapid lateral facies changes of both metasedimentary and metavolcanic rocks (Kärner, 2006). The Late Proterozoic Gariep rock successions tectonically overly the Palaeoproterozoic basement and correspond to sequences assigned regionally to the Stinkfontein and Hilda Subgroups, which include the Gumchavib, Pickelhaube, and Rosh Pinah formations. The

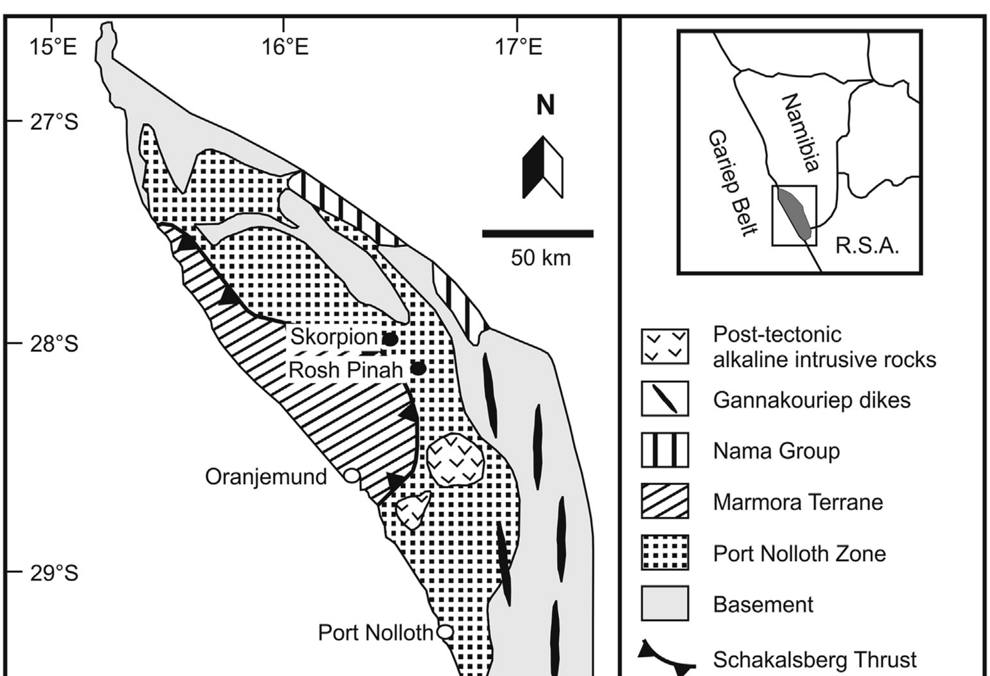

Fig. 1. Generalized geologic map of the Gariep belt in southern Namibia and northern South Africa. Both Skorpion and Rosh Pinah (filled black circles) are located within the parautochthonous Port Nolloth zone (from Borg et al., 2003; modified).