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Willemite (Zn_2SiO_4) as a possible Rb–Sr geochronometer for dating nonsulfide Zn–Pb mineralization: Examples from the Otavi Mountainland (Namibia)

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Abstract

The zinc silicate *willemite* (Zn_2SiO_4) is the main carrier of zinc in a number of high-grade, carbonate-hosted nonsulfide deposits located in the southern hemisphere that have been recently reinterpreted to be of hypogene–hydrothermal origin. The timing of willemite mineralization in these deposits is only poorly constrained. In this pilot study, willemite has been evaluated as a potential Rb–Sr geochronometer that can be used to directly date nonsulfide ore deposits. We have analyzed samples of economic-stage willemite from the Berg Aukas and Abenab West deposits, Otavi Mountainland (Namibia), which are hosted by Neoproterozoic, dolomitized and tectonized carbonate rocks. Rb–Sr elemental concentration levels and ranges of $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios in these willemite samples are comparable to those observed for the Zn sulfide sphalerite, which has been already successfully used for direct Rb–Sr dating of carbonate-hosted (MVT) deposits. This reflects similar Rb–Sr partitioning mechanisms into Zn ore minerals that precipitate either as sulfides from reduced or as silicates from oxidized hydrothermal fluids, respectively. The Rb–Sr results on willemite presented here reflect mostly low, but variable $^{87}Rb/^{86}Sr$ ratios, sufficient to generate radiogenic ^{87}Sr over time. This clearly shows that willemite is suitable as an Rb–Sr geochronometer and should be further evaluated for direct Rb–Sr dating of nonsulfide Zn deposits.

Isochron regressions combining samples from Berg Aukas and Abenab West willemites yield Rb–Sr ages in the range of ca. 500 to 560 Ma. These values are geochronologically doubtful at first sight due to high excess data scatter (MSWD = 2000 to 3000). Massive, fine-grained willemite samples from Abenab West alone ($n = 3$) give a – still statistically unacceptable (MSWD = 60) – isochron regression corresponding to an Rb–Sr age of 574 ± 84 Ma. More reliable ages are obtained from two statistically adequate small-scale Rb–Sr isochron regressions for samples of coarse-grained, well-crystallized Berg Aukas willemite, which yield 499 ± 63 Ma (MSWD = 2.6) and 493 ± 2 Ma (MSWD = 1.2), respectively.

Regardless of the quality of isochron regressions in terms of MSWD, the Rb–Sr ages obtained in this study are fully compatible with other available geochronological data that reflect distinct tectonothermal events in the study area. Therefore, on a regional scale, they appear to be at least geologically reasonable, which has yet to be verified by further studies. Comparable mineralization ages in the range of ca. 490 to 550 Ma are also reflected by the few other known economic, hypogene willemite deposits in the

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southern hemisphere, for which direct geochronological information is mostly lacking. This may point to a global period of hydrothermal activity in the Cambrian to Lower Ordovician under conditions that favored the formation of hypogene nonsulfide Zn mineralization.

Keywords: Nonsulfide deposits; Willemite; Geochronology; Rb–Sr; Namibia

1. Introduction

Oxidized ores from nonsulfide Zn–Pb deposits were the prime source for zinc metal production for hundreds of years but lost their significance during the early 20th Century due to the development of flotation and smelting techniques for zinc sulfides. During the last years, however, nonsulfide Zn–Pb deposits have gained renewed attention and are now considered to be of major importance for the future production of zinc metal (e.g., + Large, 2001; Hitzman et al., 2003 and references therein). They may contain huge reserves of high-grade ores, are easy to exploit, and their ores can now be efficiently processed using improved hydrometallurgical techniques (e.g., Woollett, 2005). Many carbonate-hosted nonsulfide Zn–Pb deposits, especially in the southern hemisphere, contain the zinc nesosilicate *willemite* (Zn_2SiO_4) in economic concentrations (Hitzman et al., 2003). Willemite was discovered for the first time in 1829 in a "calamine" orebody in Belgium, scientifically described by A. Lévy (1843) and dedicated to King Willem of Orange. It is one of the very few silicate minerals that have a trigonal–rhombohedral symmetry (e.g., Simonov et al., 1977). The average density of willemite is 4.05 and its color varies from transparent to red–brown and black. It occurs as thin, transparent, mm-sized crystals with hexagonal-prismatic terminations as well as granular masses which often replace associated primary sulfides. Therefore, willemite has been traditionally considered as a product of low-temperature supergene alteration of zinc sulfide ores. However, a number of fluid inclusion studies suggest that willemite may also form at higher temperatures (100 to 250 °C) under oxidizing hypogene–hydrothermal conditions (Sweeney et al., 1991; Brugger et al., 2003, see also Hitzman et al., 2003), both in deposits where willemite replaces primary Zn sulfides and in entirely nonsulfide mineralization styles. In fact, most carbonate-hosted economic willemite deposits in the southern hemisphere (Vazante, Brazil, ca. 28.5 Mt @ 18% Zn; Kabwe and Star Zinc, Zambia, ca. 13 Mt @ 20 to 25% Zn; Berg Aukas and Abenab West, Namibia, ca. 3.5 Mt @ 15 to 25% Zn; and Beltana, Australia, ca. 0.86 Mt @ 38% Zn, see Hitzman et al., 2003) are now interpreted to be of hypogene–hydrothermal origin (Large, 2001; Brugger et al., 2003; Groves et al., 2003; Hitzman et al., 2003). According to Brugger et al. (2003) and Hitzman et al. (2003), the precipitation of willemite, instead of sphalerite, from saline hydrothermal fluids is preferred under oxidizing (hematite-stable) conditions at neutral to basic pH, low *a* HS^- and elevated temperatures (>100 to 150 °C).

The fact that economic willemite concentrations may have formed by hypogene–hydrothermal processes and are not necessarily associated with preexisting zinc sulfides has ultimate implications for successful exploration strategies, as these may largely depend on the predictions provided by genetic models developed for these deposits (Brugger et al., 2003). It is therefore crucial to understand the geological factors that control the formation of willemite deposits in the presence or absence of known primary zinc sulfide accumulations, i.e., whether these nonsulfide ores have formed by supergene or hypogene–hydrothermal processes, or a combination of both.

For any viable genetic concept, a good knowledge on the age of mineralization is of critical importance. With a few exceptions (e.g., Dejonghe and Boni, 2005; Monteiro et al., 2006), little is known about the actual timing of willemite mineralization relative to the age of associated "primary" deposits as well as in the absence of preexisting sulfide orebodies. Radiometric dating of ore-stage minerals is the prime tool to study these aspects and thereby could decisively help to better understand the genesis of nonsulfide Zn–Pb mineralization. As with other types of economic mineral deposits, determining numerical ages for nonsulfide Zn–Pb mineralization is a difficult task, as there are no major ore phases known in these deposits that are *a priori* amenable to direct radiometric dating using conventional isotopic systems. In a recent study, Groves et al. (2003) presented K–Ar ages of 437±5 and 430±5 Ma, respectively, obtained for late-mineralization stage coronadite ($MnPbMn_6O_{14}$) from the Beltana willemite deposit located in the northern Flinders Ranges (Australia), which point to a minimum age of this mineralization during the early Silurian.

In this study we have evaluated the mineral willemite as a possible Rb–Sr geochronometer that may be useful for direct dating of nonsulfide Zn–Pb mineralization. We present some Rb–Sr data for willemite from two