Intermediate members of the lime-monteponite solid solutions (Ca$_{1-x}$Cd$_x$O, x = 0.36–0.55): Discovery in natural occurrence

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ABSTRACT

Lime-monteponite solid solutions [(Ca,Cd)O ss] with 58.5–73.3 wt% CdO were discovered as an accessory phase in medium-temperature combustion metamorphic (CM) spurrite-fluorellestadite/fluorapatite marbles from central Jordan. The type locality is situated in the northern part of the Siwaqa complex (Tulul Al Hammam area), the largest area of the “Mottled Zone” Formation in the Dead Sea region. The marbles were derived from bitumen-rich calcareous marine sediments of the Muwaqqar Chalk Marl Formation, which have high Cd, Zn, U, and Ni enrichments and contain Cd-rich wurtzite and sphalerite. Oxidative sintering of these sediments at 800–850 °C gave rise to unusual oxide accessories: lime-monteponite solid solutions, Cd-bearing Ca and Zn aluminate—tululite, zincite, and Zn-, Ni-, and Cu-rich periclase. Cadmium incorporation into different oxides was controlled by steric factors, while Cd$^{6+}$ → Ca$^{6+}$ was the principal isomorphic substitution. The intermediate members (Ca$_{0.645}$Cd$_{0.355}$)O–(Ca$_{0.453}$Cd$_{0.547}$)O with a halite-type structure have a cadmium incorporation ratio (KCd = Cd$_{\text{mineral}}$/Cd$_{\text{rock}}$) of about 843 and are the main sites for cadmium in CM marbles. In supergene environments, at low water/rock ratios, (Ca$_{1-x}$Cd$_x$)(OH)$_2$ ss (x ≤ 0.5) constitute the main secondary phase after (Ca,Cd)O ss. At higher water/rock ratios and in the presence of Cl$^-$ and F$^-$ in the solutions, calcium, and cadmium precipitated as separate phases {fluorite (CaF$_2$) and basic cadmium chloride [Cd(OH)$_{2-x}$Cl$_x$]}$. A part of cadmium becomes retained in calcium silicate hydrates. The common occurrence of anhydrous (Ca,Cd)O grains in natural rocks, only partly altered to (Ca,Cd)-hydroxide after at least 100 ka exposure to weather and climate, proves that both phases are effective long-term Cd immobilizers.

Keywords: Lime-monteponite CaO-CdO solid solution, cadmium enrichment, hydrous alteration, combustion metamorphism, central Jordan

INTRODUCTION

The upper crustal abundances of Cd and Zn are 0.09 and 67 ppm, respectively, and the Cd/Zn ratio is 0.001 (Rudnick and Gao 2003). Since cadmium is similar to zinc in its crystal-chemistry and geochemical behavior, it is hosted chiefly by sphalerite and fails to form commercially viable deposits (Ye and Liu 1999; Schwartz 2000; Ye et al. 2012). Worldwide, the average cadmium to zinc ratio is about 1/400 in zinc ores. The mean contents of Cd in sphalerites range between 0.2 and 0.6 wt% (Ye and Liu 1999; Schwartz 2000). Cadmium content is much higher in sedimentary-exhalative (SedEx) and Besshi-type volcanic massive sulfide deposits (up to 1.0–2.5 wt% Cd in sphalerite). The highest cadmium concentrations up to 5 wt%, with an average of 1.4 wt% Cd are reported in sphalerite from the carbonate-hosted Mississippi Valley-type (MVT) Zn-Pb deposits, where the low-S$^2-$ activity favored the formation of Cd-rich sphalerite (Schwartz 2000; Ye et al. 2012). Besides sphalerite, Cd has been occasionally found as impurity in tetrahedrite (Pattrick and Hall 1983; Dobbe 1992), freibergite (Pattrick 1978), or the metacinnabar-variety saukovite (Hg,Cd)S, considered an intermediate member of the metacinnabar-hawleyite series (Fleischer 1966). The few known cadmium minerals (27 mineral species) are: sulfides and sulfosalts (11), phosphates and arsenates (6), sulfates and selenates (7), carbonates (1), and native elements (1). The relatively common minerals are greenockite (CdS, hexagonal) and otavite [Cd(CO$_3$)]. Cadmium minerals {greenockite, otavite, monteponite (CdO), cadmoselite (CdSe), hawleyite (CdS, cubic), native cadmium, and niedermyrite [Cu$_2$Cd(SO$_4$)$_2$]$_4$(OH)$_{24}$H$_2$O]} occur in the zone of chemically weathered sulfide zinc ores. Their presence can be attributed to Zn scavenging by secondary smithsonite (ZnCO$_3$) and/or hemimorphite [Zn$_4$(Si$_2$O$_7$)(OH)$_2$·4H$_2$O] crystallization (Ye and