American Mineralogist, Volume 97, pages 1094–1102, 2012

Lead in zircon at the atomic scale

Masashi Kogawa,[1] E. Bruce Watson,[2] Rodney C. Ewing,[3] and Satoshi Utsunomiya[1,*]

[1]Department of Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
[2]Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180-3590, U.S.A.
[3]Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109-1005, U.S.A.

Abstract

Lead-doped zircon crystals, which were synthesized under three different conditions (Watson et al. 1997): dry at 1430 °C at atmospheric pressure without P_2O_5; wet at 900 °C at 1.5 GPa in the presence of P_2O_5; and wet at 800 °C at 1.0 GPa without P_2O_5, have been investigated to understand the mechanisms of Pb incorporation into zircon at the sub-micrometer scale, using various electron microscopy techniques including high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Four different mechanisms in which Pb may be incorporated into zircon have been identified. In the P-free synthesis, Pb-oxide hydrate particles, 50–200 nm in size, are embedded in zircon. Each Pb-particle is associated with a single vesicle, ~50 nm. Lead in the zircon structure is possibly incorporated under the detection limit value of energy-dispersive X-ray analysis (EDX) by means of: (1) $Zr^{4+} = Pb^{2+} + 2H^+$ at less than ~0.1 wt%. In the system with P, Pb-phases occur in three different forms: Pb-rich domains concentrated along cleavage planes or grain boundaries without any evident crystal form; numerous Pb-phosphate particles, as large as 100 nm, embedded heterogeneously in the zircon crystal; and homogeneous distribution of Pb in the zircon structure at less than ~1 wt% as determined by EDX. These results suggest that charge balance is maintained by the xenotime-type coupled substitution: (2) $Zr^{4+} + 2Si^{4+} = Pb^{2+} + 2P^{5+}$ with a possible minor contribution from mechanism 1. The apparent solubility limit of Pb, <1 wt%, is constrained mainly by the xenotime-type coupled substitution mechanism, which is probably due to increasing strain at higher Pb-concentrations. The presence of Pb^{2+} in natural zircon is consistent with the low-level Pb allowed by substitution mechanism 2, with only a minor contribution from substitution mechanism 1, the latter of which causes distortion in the local structure.

Keywords: Zircon, lead, TEM, nanoscale