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Formation of basic lead phases during fire-setting and other natural and man-made processes

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Abstract

Basic lead phases are relatively rare compounds occurring in various natural and anthropogenically influenced environments, most importantly those related to fire-setting (FS). The medieval FS mining method and subsequent alteration processes lead to a complex set of basic lead phases including caledonite, hydrocerussite, leadhillite, and lanarkite. Although basic lead phases have been known for over 100 years, their mode of formation and stability relations are only insufficiently known. In this study, the formation of this interesting phase assemblage is described in detail including textures, genesis, and conditions of formation. Samples include ones collected in a medieval mining district in SW-Germany and ones that underwent short-term (50 days) experiments mimicking FS and subsequent mine dump processes. The mode of occurrence and the stability relation of basic lead phases formed during FS is discussed using thermodynamic models that are adapted to also explain their occurrence in other anthropogenic and in natural environments.

Textures indicate a three step development of the FS assemblage starting with formation of cerussite during supergene weathering of primary galena prior to FS. This is followed by the decarbonization of the supergene cerussite during FS leading to the formation of lead oxides. Finally, the newly formed lead oxides were hydrated by rain and soil water in the mine dumps producing basic lead phases. Chemical composition of partially produced melt indicates that FS temperatures of up to 950 °C were reached in rare cases, whereas the lack of melt phase and predominance of litharge and lead oxycarbonates in most other samples implies that temperatures in most cases do not exceed 540 °C. Calculated stability diagrams reveal that most basic lead phases are stable at moderate to high pH and low P_{CO_2}. Thermodynamic models quantitatively explain their formation in the medieval mine dumps by the reaction of the lead oxides with a weathering fluid that increases pH and consumes CO_2 that favors the precipitation of basic lead phases. This also explains the occurrence of basic lead phases in other anthropogenic environments like slag dumps, lead contaminated soils or in contact to concrete, where the reaction of a fluid with portlandite produces high pH and low P_{CO_2}-environments. One possible explanation for the rare formation of basic lead minerals in natural oxidation zones in the absence of lead oxides is the alteration of primary galena under elevated temperatures, since the stability fields of the basic lead phases hydrocerussite and lanarkite are enlarged under elevated temperatures.

The short-term experiments show that the precipitation of basic lead phases is almost independent of the external fluid from which they precipitate. Hence, their stability is controlled by microenvironments formed at the mineral-water interface. Consequently, no closed systems in terms of CO_2 or external high pH-fluids are needed to stabilize basic lead phases in contact with lead oxides. Analyses of the experimental fluid phase show that the solubility of lead in environments, where lead oxides predominate, is mainly controlled by the basic lead phase hydrocerussite. The present study can be used to quantify the formation of basic lead phases at lead contaminated sites or in natural environments. The observations on the natural samples and the experiments show that in specific rock types, like the medieval FS ones, basic lead phases control the availability of the toxic element lead better than anglesite or cerussite over a wide pH-range. In addition, the described FS phase assemblage can help mining archeologists to understand the details of the FS method even without mining traces and provide constraints on temperatures reached during this process.

Keywords: Basic lead phases, fire-setting, stability relation, leadhillite, lanarkite, hydrocerussite, caledonite