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LEAD IONS AND EMPTY HALIDE SITES IN APATITES

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ABSTRACT

It is shown from experimental evidence and on theoretical grounds that oxypyromorphite and silicate pyromorphite do not contain Pb^{4+}. The formulae of these compounds are $Pb_{10}(PO_4)_6O$ and $Pb_{10}(PO_4)_4(SiO_4)_2$ resp.; they are in agreement with the assumption of void halide sites occurring in the apatite structure.

INTRODUCTION

In a recent paper one of us (J. Ito (1968)) raised the question whether apatites with totally or partly empty halide places do occur. Ito considered especially the compounds oxypyromorphite and silicate-pyromorphite, the formulas of which have been given earlier by Merker and Wondratschek (1960, 1956) as $Pb_{10}(PO_4)_6O$ and $Pb_{10}(PO_4)_4(SiO_4)_2$, resp. These authors had assumed voids to occur at the halide sites. According to his investigations Ito (1968) came to the conclusion that these formulas may be rewritten as $Pb_9{}^{2+}Pb^{4+}(PO_4)_6O_2$ and $Pb_8{}^{2+}Pb_2{}^{4+}(PO_4)_4(SiO_4)_2O_2$, resp., with fully occupied halide sites and Pb^{4+} in the structure. Other compounds have been considered in a similar way, *e.g.* $Pb_5{}^{2+}Pb_3{}^{4+}Y_2(SiO_4)_6O_2$. It is the purpose of the present paper to clarify this situation.

EXPERIMENTAL RESULTS AND THEORETICAL CONSIDERATIONS

Oxypyromorphite (oxy), silicate-pyromorphite (sil), and a product of composition 3 oxy×1 sil have been dissolved in cold 2 n HNO_3. No residue of black PbO_2 could be observed. Generally compounds containing Pb^{4+} give this residue, *e.g.* $Pb_3O_4 = Pb_2{}^{2+}Pb^{4+}O_4$. The above mentioned result therefore is a qualitative proof for the absence of Pb^{4+}.

Pb^{4+} has been determined quantitatively. To 0.5 g of the compound to be tested and to 7 g NaI, which has been placed together in a glass-stoppered flask, 10 ml of 2 n HCl was added. The flask remained closed until dissolution was complete. Then an aqueous solution of 1.5 g EDTA (disodium salt) and 3 g sodium acetate was added. The lead was bound in the complex and the subsequent titration of the newly formed iodine with thiosulfate was not affected by the precipitation of the yellow PbI_2. For Pb_3O_4 this method gave the correct amount of tetravalent lead.

When the three compounds referred to above were titrated with 1/10 n thiosulfate-solution, about 0.2 to 0.3 ml were used up in each case. Test samples with no Pb^{4+} gave the same values. A compound of composition $Pb_8^{2+}Pb_2^{4+}(PO_4)_4(SiO_4)_2O_2$, however, would require 7.50 ml and one of composition $Pb_9^{2+}Pb^{4+}(PO_4)_6O_2$ 3.74 ml thiosulfate solution.

It follows that the compounds mentioned do not contain any chemically perceivable amount of Pb^{4+}. The solutions of the three compounds in the presence of NaI and HCl were always of an orange-yellow color. This color is caused by Pb^{2+}-iodo-complexes and by very small amounts of iodine, which is formed by oxydation of the acid solutions by oxygen from the air. This explains why some thiosulfate is used up in the titration. Solutions with greater amounts of iodine are of an intensive brown color. The orange color, therefore, is no indication of Pb^{4+}.

The pyromorphites in question are prepared from the melt at temperatures higher than 1000°C. In compounds with basic oxides Pb^{4+} is in some cases stable to high temperatures (see *e.g.* Scholder, Räde and Schwarz (1969)). On the other hand, compounds of Pb^{4+} with the acid oxides P_2O_5 and SiO_2 which are stable at temperatures higher than 300°C are not known.

$Pb_{10}(PO_4)_4(SiO_4)_2$ has been found as compound with a very large field of stability in the system $PbO–SiO_2–P_2O_5$, Paetsch and Dietzel (1956). Similarly $Pb_{10}(PO_4)_6O$ occurs as incongruently melting compound in the system $PbO–P_2O_5$, Merker and Wondratschek (1960). The conditions of synthesis and the occurrence in these systems point to the formulas given in these papers. The small weight losses during preparation support this too.

Compounds containing ions of the same element in different oxidation states are deeply colored in general because of charge-transfer (*e.g.* Pb_3O_4); yet the above-mentioned compounds are colorless.

CONCLUSIONS

From all these results there follows that the compounds in question do not contain Pb^{4+}. The observations are in agreement with the assumption of all the lead being divalent and of void halide sites occurring in the apatite structure.

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COLLOFORM HYDROTHERMAL MUSCOVITE ("CHACALTAITE")

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Abstract

An analysis of a $2M_1$ polytype of fibrous colloform muscovite from a low temperature hydrothermal vein occurrence at Chacaltaya, Bolivia, gave: Na_2O 0.31, K_2O 10.14, Rb_2O 0.12, Cs_2O 0.01, CaO 0.04, BaO 0.05, Li_2O 0.12, MgO 1.06, FeO 2.46, MnO 0.06, Fe_2O_3 1.04, Al_2O_3 32.09, SiO_2 47.56, TiO_2 0.05, H_2O- 0.14, H_2O+ 3.86, F 1.37, O=F 0.58, total 99.90. Specific gravity 2.84; $d(005)$ 1.9975 Å: β 1.584, γ 1.590, $2V$ 45°. The material had earlier been described by Kolaczkowska (1936) as an independent species, here discredited.

The occurrence of muscovite in hydrothermal veins at Chacaltaya, near La Paz, Bolivia, in the unusual form of fibrous colloform crusts has been noted by Thugutt (1936, 1964) and by Ahlfeld and Reyes (1938). A specimen from the Ahlfeld collection is described here. It consists of pale yellowish gray crusts up to several cm thick composed of concentric layers (Fig. 1). The surface of the crusts is botryoidal with a smooth, almost polished appearance and a waxy luster. The individual layers are easily separable and range up to about 1 mm in thickness. They are composed of fibers or laths, visible under low magnification, that are arranged with their direction of elongation, [100], perpendicular to the surface of the layers. On cross-fractures the layers have a silky luster and are translucent. Optically the mineral has $\beta = b = 1.584 \pm .001$, $\gamma = a = 1.590 \pm .001$ and 2V $(-) \sim 45°$. The measured specific gravity is 2.84.

X-ray patterns taken in Cu radiation by both film and chart techniques, employing sample mounts so prepared as to minimize preferred orientation, gave excellent muscovite patterns of the $2M_1$ type. Interplanar spacings determined with the aid of Si as internal standard gave $d(005) = 1.9975$ Å $\pm .0010$ and $d(006) = 1.6634$ Å $\pm .005$ [lower precision because of poor line quality].

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