European Mineralogical Conference
Vol. 1, EMC2012-52, 2012
European Mineralogical Conference 2012

Layered Pb oxychloride minerals structurally related to litharge: general principles of classification and systematics

O.I. Siidra (1), R.W. Turner (2), S.V. Krivovichev (1), and M.S. Rumsey (3)

(1) Dept. Crystallography, Geological faculty, Saint-Petersburg State University, University emb. 7/9, 199034, St.Petersburg, Russian Federation (siidra@mail.ru), (2) The Drey, Allington Track, Allington, Salisbury SP4 0DD, Wiltshire, UK, (3) Mineralogy Department, Natural History Museum, Cromwell Road, London, SW7 5BD, UK

The number of layered Pb oxychloride minerals has increased within the last two years [1, 2]. Lead oxychlorides can be found as secondary minerals in oxidation zones of mineral deposits. Wide range of elements (As, S, V, Mo, P, Si, I, Mn etc.) may intercalate into the structures of these minerals. This makes studied class of compounds of particular interest from the geochemical point of view. The variety of layered lead oxychlorides includes the following mineral species: asisite, $Pb_7SiO_8Cl_2$; blixite, $Pb_8O_5(OH)_4Cl_2$; hereroite, $[Pb_{32}O_{20}(O,)](AsO_4)_2((Si,As,V,Mo)O_4)_2Cl_{10}$; kombatite, $Pb_{14}(VO_4)_2O_9Cl_4$; mereheadite, $Pb_{47}O_{24}(OH)_{13}Cl_{25}(BO_3)_2(CO_3)$; parkinsonite, $Pb_7MoO_9Cl_2$; rumseyite, $(Pb_2OF)Cl$; sahlinite, $Pb_{14}(AsO_4)_2O_9Cl_4$; schwartzembergite, $Pb_5IO_6H_2Cl_3$; symesite, $Pb_{10}(SO_4)O_7Cl_4(H_2O)$ and vladkrivovichevite, $[Pb_{32}O_{18}][Pb_4Mn_2O]Cl_{14}(BO_3)_8{\cdot}2H_2O$ - masterpiece of structural architecture and complexity. Layered lead oxychlorides crystal structures are based on alternation of lead-oxygen layers and halogen sheets. The structure of Pb-O layers in all known lead oxychloride minerals can be described as a derivative from the classic [OPb] layer in tetragonal modification of divalent lead oxide (litharge). These continuous [OPb] layers are formed by OPb_4 oxocentered tetrahedra. To transform the [OPb] layer in litharge into the any type of layer observed in lead oxychlorides, one has to excise certain blocks of OPb_4 tetrahedra from the former. [OPb] layers alternate with tetragonal sheets of chlorine ions. In asisite, parkinsonite, kombatite, sahlinite and hereroite the stacking sequence of sheets is ...-Cl-OPb-OPb-Cl-OPb-OPb-..., thus OPb:Cl ratio is 2:1. Another possible stacking sequence is 1:1 (...Cl-OPb-Cl-OPb-Cl...) with simple alternation of the PbO-derived layers and chlorine sheets. This type of structural architecture has been observed in rumseyite, symesite, schwartzembergite, blixite, mereheadite, vladkrivovichevite. Since ideal [OPb] layers are electroneutral and chlorine sheets are negatively charged, the structure requires a charge-balance mechanism to compensate for the negative charge of the Cl-layers. This may be achieved via five different schemes:

1. Substitution of PbO groups in the [OPb] layer by tetrahedral anions: SO_4 (symesite), MoO_4 (parkinsonite), VO_4 (kombatite), AsO_4 (sahlinite), SiO_4 (asisite), etc. Note, the substitution is disordered in parkinsonite and asisite. In symesite, kombatite, sahlinite and hereroite the vacancies in the PbO-type layers have the forms of squares and/or a double square.

2. $O^{2-} \leftrightarrow OH^-$ substitution mechanism in the [OPb] layers. Three oxygen anions are replaced by two hydroxyl anions in the structure of blixite. The vacancies have a form of an elongated rectangle.

3. Combination of substitution of PbO groups in the [OPb] layer by triangular TO_3 groups (T = B, C) with the formation of square shaped vacancies, $O^{2-} \leftrightarrow OH^-$ substitution resulting in the formation of elongated rectangle and insertion of additional Pb sites within the sheets of Cl^- in the structure of mereheadite.

4. Insertion of $[OPb_4Mn_2(BO_3)_8Cl_2]$ clusters into both PbO-type and halogen layers in the crystal structure of vladkrivovichevite.

5. Fluorine as a charge compensating agent in mixed O/F anioncentered tetrahedra in rumseyite.

The above mentioned structural features allow to propose for the recognition of the separate group of minerals, containing a number of sheet oxychloride minerals with similar and related structures derived from litharge (tetragonal PbO).

Acknowledgements

This work was financially supported by the President of Russian Federation grant for young scientists (# MK-5074.2011.5) and St. Petersburg State University through the internal grant 3.37.84.2011.

References

[1]. Turner, R., Siidra, O.I., Rumsey, M.S., Krivovichev, S.V., Stanley, C.J., Spratt, J. (2012) Hereroite and vladkrivovichevite – two novel lead oxychlorides from the Kombat mine, Namibia. Mineralogical Magazine, accepted.

[2]. Turner, R., Siidra, O.I., Krivovichev, S.V., Stanley, C.J., Spratt, J. (2012) Rumseyite, $[Pb_2OF]Cl$, the first naturally occurring fluoroxychloride mineral with the parent crystal structure for layered lead oxychlorides. Mineralogical Magazine, accepted.