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Research paper

Crystallochemical aspect of clay and clayish matter minerals luminescence

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ABSTRACT

X-ray luminescence (XRL) spectra in optical range of wave-lengths and thermoluminescence (TL) curves of several clay and clayish matter minerals were recorded for the first time. Mineral composition of all the samples was determined on the base of X-ray diffraction results. It was stated that XRL of clay minerals is related to their crystallochemical characteristics (type and degree of regularity of structure and isomorphism occurrence in particular). In the opinion of the authors, differences between luminescent characteristics of halloysite and kaolin minerals are related to syngony (triclinic or monoclinic) and possibility of Si^{4+} substitution with Al^{3+} in tetrahedral coordination that lead to uncompensated charges appearing and formation of luminescence centres based on silicon and aluminium tetroxides.

1. Introduction

Clay minerals are widely spread in weathering matter of rocks and ore deposits (Chamley, 1989; Muller et al., 2001; Velde and Meunier, 2008). They make up loose or dense aggregates, which usually contain not only one but a number of clay minerals and oftentimes minerals of other compounds classes. Definition of mineral composition of such fine-grained polymineralic matter with separation of each mineral monofraction by means of common methods is quite difficult. However it is necessary for solving problems of genesis as well as strictly practical issues. Clay minerals determination usually takes the leading part in paleoclimatic studies (Guyot et al., 2007; Hallam et al., 1991; Muller et al., 2001), in petroleum investigations (Shumskayte, 2013). Depending on structure (that determines species) clay minerals may have rather different technical characteristics, e.g. different levels of adsorption ability (Wu et al., 2013). According to this, different industries apply them. Sometimes it's ceramics production or nano-technologies (Pasbakhsh et al., 2013; Wang and Wang, 2016; Yuan et al., 2015; Zhou and Keeling, 2013; Zhou et al., 2016), sometimes petroleum industries (Shumskayte, 2013) and so on. Some of clay minerals even might be ore ones (Boroznovskaya et al., 2015). Therefore mineral composition analysis precedes evaluation of clays practical importance. Moreover, clay minerals presence in ores may have negative effects, which express in worsening of technological properties like it happens sometimes with nonferrous metals ores (Boroznovskaya et al., 2015). At the same time some other minerals as sulfates of copper and lead, which visually resemble clay minerals, are into the category of secondary ore minerals. Thus, taking visual similarity of clay minerals and some other compounds (e.g. several sulfates) with other properties and practical value in consideration, importance of mineralogical analyzing of clays becomes obvious.

Traditionally in geologic practice X-ray diffraction and thermal analyses are used for clays mineral composition studies. But using these methods require specific (sometimes laborious and long) samples preparation; also not all the time it is possible to interpret the results clearly. Luminescence analysis of clays may be the complimenting one. It requires small samples and is much less laborious than X-ray diffraction and thermal analyses, sensitive and express enough.

The purposes of the work is to record X-ray luminescence spectra of minerals of clay and clayish matter, to show the possibility of clay minerals crystallochemical features influence on their luminescent properties and to show the possibility to use luminescent properties as diagnostic ones for polymineral clay and clayish matter composition determination.

2. Materials and methods

Objects of the study were clay minerals from collection of mineralogical museum of Tomsk State University, clays and clayish matter of Rubtsovsky polymetallic ore area (Ore Altai) and clay component of sedimentary rocks of reservoirs of South-Pestsovaya petroliferous area (West Siberia).

Clay minerals belong to the family of phyllosilicates and contain continuous two dimensional tetrahedral sheets of composition T_2O_5

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(T = Si, Al, Fe^{3+}, etc.) with tetrahedra linked by sharing three comers of each, and with the fourth corner pointing in any direction. The tetrahedral sheets are linked in the unit structure to octahedral sheets, or to groups of coordinated cations, or individual cations. There are minerals made up of layers of one or another type (Brigatti et al., 2006; Guggenheim et al., 2006).

First type layers are so called 1:1 layers consisting of one tetrahedral sheet built of silicon tetroxides and octahedral (gibbsite-like) sheet built of octahedra consisting of aluminium and oxygen ions and hydroxyl groups. These sheets are electrostatically compensated (Hu and Yang, 2013). Such is the structure of kaolinite and its polytypes: dickite and nacrite. Halloysite is a mineral with composition and structure alike to those of kaolinite and its polytypes: dickite and nacrite with common formula $Al_4[Si_40_{10}][OH]_8$. Difference between halloysite and kaolinite is presence of molecular water between two-sheet layers in structure of halloysite (Yuan et al., 2015). Also halloysite crystallize in monoclinic system (P).

Serpentine group minerals structures also are made of “1:1 layers”. Pecoraite is a nickel analogue of clinochrysotile with formula $Ni_6[Si_4O_{10}](OH)_8$, so it belongs to serpentine group. It's a phyllosilicate composed of tetrahedral silica sheets and octahedral brucite type sheets. There are hollow tubular structures due disparity of tetrahedral and octahedral sheets (McDonald et al., 2009).

2:1 layers are ones consisting of two tetrahedral sheets and one octahedral sheet between them (Brigatti et al., 2006; Li et al., 2016). Smectites are among phyllosilicates consisting of such layers. Montmorillonite belongs to smectites. Part of Si^{4+} ions from silicon tetroxide sheets may be substituted by Al^{3+} and at the same time part of Al^{3+} from alumohydroxyl octahedra may be substituted by Fe^{3+} or Mg^{2+} and Fe^{2+}. Herewith SiO_2/Al_2O_3 ratio varies much. Uncompensated isomorphic substitutions produce excess negative charge, which is compensated by interlayer K^+, Na^+, Mg^{2+}, Ca^{2+} and H_3O^+ cations inclusion (Scholtzova et al., 2014; Shi et al., 2013). In structure of montmorillonite all the tetrahedra are occupied by silicon cations while some of Al^{3+} cations in octahedra are isomorphically substituted with Fe^{2+} or Mg^{2+} (occasionally with Fe^{3+}). Consequently, charges balance is upset (it's restored by interlayer M^+ cation) and negative charge concentrates within octahedral sheets herewith. Unlike it is in montmorillonite, in structures of beidellite and nontronite negative charges concentrate within tetrahedral sheets (Frost et al., 2002).

Theoretical composition of nontronite, which crystallizes in monoclinic system, is $Na_{0,33}\{Fe_2[(Al_{0,33}Si_{3,67})_4O_{10}](OH)_2\}^{-0,33}\cdot nH_2O$. Real composition of nontronite is unstable and approximate to theoretical one infrequently. Usually nontronite contain significant quantities of Al_2O_3 (up to 14%), MgO (up to 8%), CaO (up to 2%) and small amounts of K_2O, Na_2O, sometimes NiO, Cr_2O_3. Raw nontronite usually has intermediate composition between theoretical nontronite composition and montmorillonite composition. Besides, nontronite belongs to miscibility row with beidellite ($(Na,Ca)_{0,3}Al_2[(Si,Al)_4O_{10}](OH)_2\cdot nH_2O$).

Palygorskite is a hydrous phyllosilicate of aluminium and magnesium with admixture of calcium and some other elements. Its formula is $Ca_y(H_2O)_4\{Al_{2x}Mg_{5-3x-y}[Si_4O_{10}]_2(OH)_2\}\cdot 4H_2O$. Its structure includes ribbons of 2:1 phyllosilicate structure connected by Si—O bonds (Brigatti et al., 2006).

Predominantly light-coloured with grayish, greenish and brown tones incoherent aggregates were meant by the term “clayish matter”. While studying such matter it was stated that it often has complicated mineral composition, including not only exactly clay minerals (kaolinite group minerals, smectites, hydromicas or interlayer-deficient micas, chlorites, etc.), but also sulfate minerals (alunite, osarizawaite, beaverite). Endogenous and supergene clayish matter is widespread within primary ores and oxidized zones of Rubtsovskoe, Zakharovskoe and Stepnoe polymetallic ore deposits, which belong to Rubtsovsky ore area of Ore Altai (Boroznovskaya et al., 2015). That matter may be a part of ore aggregate and influence on its technological properties.

X-ray diffraction analysis was carried out with use of X-ray diffractometer XPert PRO. X-ray tube with copper anode ($\lambda_{k\alpha}$ = 1,5418 Å) was used as a radiation source. Analysis was carried out in 2Θ angles range from 4 to 60°. Scanning step was 0.02°, scan speed was about 0.066°/s. Soller slit width was 1/8°. Samples preparation consisted of mechanical disintegration to particles size less than 0.001 mm and making of oriented aggregate.

X-ray luminescence (XRL) spectra in optical range of wave lengths from 200 to 500 nm were recorded for all the minerals. XRL analysis was carried out with use of unit, which was built on the basis of MDR-12 monochromator and FEU-100 photomultiplier, and with computer processing of analysis results according to previously outlined method (Boroznovskaya et al., 2016). X-ray tube with Mo-anticathode BSV-2 of URS-55 apparatus was a source of excitation.

3. Results and discussion

3.1. X-ray diffraction and luminescence of minerals of kaolin group

3.1.1. X-ray diffraction analysis results

Studied clay minerals were recognized through basic reflections at the diffractogram with use of PDF-4 (ICDD data base – International Centre for Diffraction Data) (Table 1).

In addition preliminary samples heating to 550 °C for 2 h was carried out. This was made with the view of confirmation of X-ray diffraction analysis results, because in case of kaolin minerals such step led to full disordering of the structure and disappearing of most reflections at newly recorded diffractogram (Fig. 1).

3.1.2. X-ray luminescence analysis results

The structure of kaolin minerals makes isomorphic substitutions uncommon but still possible (He et al., 2011). Exactly these occasional substitutions of Si^{4+} with Al^{3+} may lead to uncompensated electric charges occurrence. This in turn leads to formation of luminescence

Table 1
Main diffractional characteristics of clay and clayish matter minerals.

Mineral	Main reflections, Å (intensity, relative units)	Number in PDF-4
Kaolin minerals		
Kaolinite	**7,15(10)**-3,57(8)-	01-075-0938
$Al_4[Si_4O_{10}](OH)_8$	2,36(8)-4,44(5)	
Dickite	**7,18(10)-3,59(7)**-	00-058-2002
$Al_4[Si_4O_{10}](OH)_8$	4,13(6)-2,33(6)-3,80(4)	
Nacrite	**7,14(10)**-4,33(8)-	00-016-0606
$Al_4[Si_4O_{10}](OH)_8$	3,56(8)	
Halloysite group minerals		
Halloysite	**4,41(10)**-7,42(5)-	00-029-1487
$Al_4[Si_4O_{10}](OH)_8\cdot 4H_2O$	3,62(5)-2,56(4)-2,40(2)	
Montmorillonite group minerals		
Montmorillonite	**14,2(10)**-4,45(7)-	00-060-0318
$(Al,Mg,Na)_2(OH)_2[Si_4O_{10}]\cdot 4H_2O$	3,52(3)	
Nontronite	**14,31(10)**-	00-034-0842
$(Fe,Al,Na)_2(OH)_2[(Si,Al)_4O_{10}]\cdot 4H_2O$	4,50(8)-2,61(5)	
Other clay minerals		
Palygorskite MgCa	**10.47(10)**-4.46	01-081-8599
$(Al,Fe)_2(OH)_2[Si_4O_{10}]_2\cdot 8H_2O$	(2)-2.50(5)	
Pecoraite	**7,31(10)**-3,61(8)-	00-049-1859
$Ni_6[Si_4O_{10}](OH)_8$	1,50(8)	
Sulfates of clayish matter		
Osarizawaite	**5,75(8)**-3,52(6)-	00-015-0178
$Pb(Al_2Cu)[SO_4]_2(OH)_6$	**3,00(10)**-2,87(5)-2,84(5)-1,92(5)	
Alunite	4,95(6)-**2,98(10)**-	00-001-0879
$KAl_3[SO_4]_2(OH)_6$	3,50(5)-**1,90(5)**	