RENTGENSKA DIFRAKCIJA GLIN

Priprava vzorca

- odvisna od sestave
- možnost ireverzibilne reakcije v vzorcu

Dispergiranje

- gline so drobnozrnate ($2r < 2\mu m$),
- topne soli (Fe minerali, organske snovi) jo flokulirajo
- deflokulanti: NH_3, Na-tripolifosfat

Separacija

- delci >1 μm so neglineni: kremen, glinenci, karbonati, debelozrnata sljuda
- ultracentrifuga za drobnozrnato frakcijo
- sedimentacijska separacija (centrifugiranje v vodni suspenziji): vodo odsesavamo ali izparevamo

Segrevanje vzorca

- na steklenem nosilcu do 550 ^oC
- na srebrnem nosilcu do 900 ^oC ⇒ dehidracija ⇒ visokotemperaturna kamera

Nosilci vzorcev

- kapilara
- steklena palčka
- Al, Pt nosilci z vdolbino

Priprava vzorca za rtg difrakcijo

- zmlet vzorec (<1 μm)
- orientirani vzorci: dobimo samo uklone {00l} serije, manj važnih {hkl} uklonov pa ne
- vzorec sedimentiramo, centrifugiramo na nosilec
- neorientirani vzorci:
    - nosilec polnimo od strani,
    - granuliranje vzorca z org. snovjo.

Tehnike rtg difrakcije glinenih vzorcev

- gline so slabo kristalinične ⇒ široki piki
- gline z Fe < 5 mas.% analiziramo s Cu anodo
- gline z Fe >5 mas.% analiziramo s Co anodo
- nastavitev števnega difraktometra:
    - $v_{snemanja} = 1^o$ (2θ)/min,
    - $v_{papirja} = 1^o(2\theta)$/cm,
    - $2\theta = 2 - 65^o$
- monokromatski $Cu_{K\alpha}$ žarek
- kalibracija s kremenom in alkoholom
- analiza d vrednosti, ker niso odvisne od λ (muskovit)

Določanje mineralne skupine

- uporabimo uklone {00l} (tabela 2)
- paligorskit {110}, d = 10,5 Å
- sepiolit {110}, d = 12,2 Å
- vzorce obdelujemo z
    - glicerolom,
    - etilenglikolom (smektiti),
    - segrevamo, da dehidrirajo (hidroksidi, kaolinit) (tabela 1)

Tabela 2: lege uklonov ploskev (00l) in intenzitete za posamezne skupine glinenih mineralov

Minerals	d (001)	I (00l) l = 1	2	3	4	5	d (060)
Kaolinite group	7·15–7·20	100	90	15	10	4	1·489
Mg-serpentine	7·25–7·35	100	100	—	20	20	1·536–1·540
Fe-serpentine	7·04	100	100	—	—	5	1·555
Berthierine							
Pyrophyllite	9·20	80	30	100	5	10	1·493
Talc	9·35	vs	w	s	vw	m	1·527
Smectites							
(dioctahedral)	←		variable			→	1·49–1·50
(trioctahedral)	←		variable			→	1·52–1·54
Vermiculite	14·3	100	10	15	30	40	1·541
Muscovite	10·0–10·05	>100	55	>100	20	75	1·499
Phlogopite	10·0–10·05	>100	20	>100	30	65	1·538
Biotite	10·0	100	20	90	10	10	1·530
Celadonite	9·95	50	—	70	—	10	1·510
Glauconite	9·95	100	—	60	—	20	1·511
Paragonite	9·62	30	20	100	—	30	1·481
Chlorites (magnesian)	14·15–14·35	70	100	50	80	30	1·549
Chlorite (iron-rich)	14·10–14·25	20	100	20	50	10	1·560

Sepiolite $d(110) = 12{\cdot}1$–$12{\cdot}3$, $I = 100$; $d(131) = 4{\cdot}30$, $I = 25$–40.
Palygorskite $d(110) = 10{\cdot}4$–$10{\cdot}5$, $I = 100$; $d(121) = 4{\cdot}25$, $I = 10$–30.

Tabela 1: spremembe lege uklonov v odvisnosti od načina tretiranja vzorca

Mineral	Air-dried	Ethylene glycol	300–350°C	500–600°C	Reflection disappears at	Remarks	Reference
Imogolite	20–12 Å (B)	20–12 Å (B)	19	Disappears	300–450°C	20–12 Å band replaced by sharp intense 19 Å reflection at 100–200°C; reversible in moist air	
Kaolinite	7	7	7	Disappears	500–550°C	Occasionally weak broad band at 12–14 Å at 500–550°C	
Dickite	7	7	7	[illegible]	[illegible]	[illegible] 550–700°C	[illegible]
Nacrite	7	7	7	Disappears	550–650°C		
Kaolinite, disordered	7	7	7	Disappears	500–550°C		
Halloysite-7 Å	7	7	7	Disappears	450–520°C		
Halloysite-10 Å	11	10	7	Disappears	450–520°C	Dehydrates, usually irreversibly to 7 Å form at 50–100°C	
Serpentine	7	7	7	Disappears	575–700°C	Broad reflection 11–14 Å region at 550–650°C; forms olivine and enstatite at 650–700°C	(2, 3)
Nepouite	7 (B)	7 (B)	7 (B)	Disappears	550–600°C	Broad reflection 11–14 Å at 550–650°C; amorphous 550–800°C; NiO-like phase 800–1000°C	(3, 4)
Berthierine (ferrous)	7	7	7	Disappears	450–500°C	Oxidized to ferric form 350–450°C	(5)
Berthierine (ferric)	7	7	7	Disappears	450–500°C	Forms hematite + spinel 650–1000°C	(5)
Cronstedtite	7	7	7	7		Spinel-like phase with 7 Å reflection persists to >700°C	(6)
Amesite	7	7	7	Disappears	550–600°C		(7)
Mica	10	10	10	10	800–1000°C+		
Kerolite–pimelite	10 (B)	10 (B)	10 (B)	10 (B)	700–800°C	Transformed to enstatite 700–800°C	(4)
Smectite, Mg, Ca	15	17	10	10	700–1000°C	Trioctahedral varieties more stable in 700–1000°C range	
Smectite, Na	12·5	17	10	10			
Vermiculite, Mg, Ca	14·5	14·5	10	10	700–1000°C		
Vermiculite, Na	12·5	14·5	10	10			
Chlorite (magnesian)	14	14	14	14	800°C	14 Å intensity increased at 500–600°C; forms olivine at about 800°C	(8)
Chlorite (iron-rich)	14	14	14	14	600°C	14 Å intensity much increased 500–600°C; forms olivine at 600–700°C	
Swelling chlorite	14	16 17	14	14			
Palygorskite	10·5	10·5	10·5 – 9·2	9·2	700°C	Marked increase in 10·5 Å intensity at 150°C	(9)
Sepiolite	12·2	12·2	12·2 – 10·4	10·4	700°C		

Temperature at which thermal changes occur are affected by size of crystals and duration of heating; larger crystals require higher temperature and longer time for reaction.

(B) = broad reflection.

References: (1) Hill (1955); (2) Brindley and Zussman (1957); (3) Brindley and Wan (1975); (4) Pham Thi Hang and Brindley (1973); (5) Brindley and Youell (1953); (6) Steadman and Youell (1957); (7) Brindley, Oughton and Youell (1951); (8) Brindley and Ali (1950); (9) Nathan (1970).

Primer:

- kaolinit {001} d = 7,1 Å {002} d = 3,58 Å
- klorit {001} d = 14,1 Å {002} d = 7,1 Å {004} d = 3,55 Å

  Klorit je topen v topli HCl (razredčeni)

Določanje mineralne podskupine

- intenziteta glavnih odbojev

Primer:

- trioktaedrična sljuda ima slabši odboj od {002} napram {001} in {003},
- dioktaedrična sljuda pa ne

- odboj {060} pri $2\theta = 59 – 63^o$ za Cu $_{K\alpha}$
  - dioktaedr min.: d = 1,48 - 1,50 Å
  - trioktaedr min.: d = 1,53 - 1,55 Å (tabela 2)

Mešan vzorec: obdelava (separacija, koncentriranje, odtapljanje)

1. Minerali kaolinitove skupine

Značilni ukloni

	Ravnina	d (Å)
Kaolinit	{001}	7,2
	{002}	3,6
Dickit in nacrit	{002}	7,2
	{004}	3,6

Halloysit 10 Å oblika ⇒ 70^{o}C prehaja v 7 Å obliko z d = 7,2 Å.

- **Halloysit** - $Al_2Si_2O_5(OH)_4.2H_2O$
  {001} d = 10,1 Å {003} d = 3,40 Å

- **Metahalloysit** - $Al_2Si_2O_5(OH)_4$ T > 70^o C
  {001} d = 7,2 Å {002} d = 3,60 Å

- z neurejenostjo slabijo
- $2\theta = 35 – 40^o$ dvignjeno ozadje
- {060} d = 1,48 Å ⇒ diokatedričen

2. Minerali sljudine in illitove skupine

- težko ločimo med sabo
- kemična analiza:
    - 5 - 8% K_2O illit in glavkonit
    - 8 - 9 % K_2O biotit
    - 10 - 11 % K_2O muskovit
- sejalna analiza:
    - sljuda v debelozrnati frakciji muskovit in/ali biotit
    - sljuda v drobnozranit frakciji illit in/ali glavkonit

3. Minerali kloritove in vermikulitove skupine

4. Smektiti in minerali z mešanimi plastmi

- obdelava z etilenglikolom (dobimo pik pri 17 Å).

RTG difrakcija akcesornih mineralov

- jih je malo
- vidni samo najmočnejši ukloni (mineralne asociacije)

1. Železovi in aluminijevi oksidi in hidroksidi

- so pogosti v glinah
- ogrevanje (tabela 3)

Tabela 3: tretiranje železovih in aluminijevih mineralov (segrevanje)

	Decomposition temperature (1 hour in air)	Products observed by X-ray diffraction
Goethi :	230–280°C	Immediate product at 280°C is disordered hematite; well-crystallized hematite gradually develops with further heating to 900°C.
Al-goe ıite	240–350°C	Immediate product at 350°C is disordered Al-hematite; well-crystallized hematite with cell dimensions near normal Al-free hematite develops at about 900°C.
Lepido rocite	230–280°C	γ-Fe_2O_3 with broad reflections which transforms to normal hematite at 400–500°C; disordered hematite if formed does not persist.
Maghe ıite	350–450°C	Normal hematite.
Magne te	600–800°C	Hematite.
Akaga ëite	200–400°C	Pattern of akaganéite gradually weakens; at about 420–500°C normal hematite pattern appears.
δ-FeO H	140–260°C	Disordered form of hematite formed *via* goethite intermediate.
Feroxy ıyte, δ'-FeC OH	Unstable in air	Transforms to goethite in air.
Ferrihy lrite (Si free)	350–400°C	Normal hematite.
Ferrihy lrite, natur , and synt etic contain ng Si	550–600°C	Normal hematite.
Gibbsi :	150–200°C	Boehmite and χ-Al_2O_3 (see Brindley and Choe, 1961).
Bayeri :		Boehmite and feebly crystallized γ-Al_2O_3 (Rooksby, 1961).
Nordst andite		Nordstrandite probably behaves like bayerite.
Boehm .e	450–500°C	γ-Al_2O_3.
Diaspc e	470–500°C	Immediate decomposition product is disordered corundum; on further heating well-crystallized corundum gradually develops.

Korund α-Al_2O_3

- je končni produkt gretja gline
- d = 2,085 Å za {113} od korunda je referenčna intenziteta za JCPDS (Joint Committee on Powder Diffraction Standards)

Kremen

- d = 3,34 Å
- meja detekcije < 1 mas.%
- visokotemp. oblike kremena,
- amorfne oblike - opal

Glinenci

- debela zrna v glinah
- K – glinenci d = 4,2 Å
- Na - Ca glinenci d = 3,30 - 3,18 Å in d = 4,03 Å

Karbonati

Značilen najmočnejši uklon pri d = 3,03 Å za kalcit in d = 2,89 Å za dolomit

Zeoliti

- hidrati alumosilikati Na, K, Ca, Mg
- **heulandit - klinoptilolit** (monokl.)
  $(Na,K)_x(Ca,Mg)_y(Al,Fe^{3+})_{x+2y} Si_{36-(x+2y)} O_{72}.19\text{-}26H_2O$

  x = 0,3 – 6 y = 0,3 – 4 x+y = 4 – 7 x+2y = 6 - 9

  Si/Al > 4 ⇒ klinoptilolit
  Si/Al < 4 ⇒ heulandit
  ogrevanje do 450 °C za 15 ur spremeni Si/Al razmerje in količino M^{2+}

- skupina **phillipsita** (monokl.)
  $(Na,K)_x(Ca,Mg)_y(Al,Fe^{3+})_{x+2y} Si_{16-(x+2y)} O_{32}.12H_2O$

- **analcim** (kubičen)
  $Na_{17}Al_{17}Si_{31}O_{96}.16H_2O$ do $Na_{14}Al_{14}Si_{34}O_{96}.16H_2O$
  celica se mu spreminja s temperaturo.

Minerali, nastali pri žarenju glin T > 900 °C

- sillimanit - $Al_2O_3.SiO_2$
- mullit - $3Al_2O_3.2SiO_2$

Določanje stopnje urejenosti v strukturah 1:1

Kaolinit

- {001} 2θ = 12,4° d = 7,15 Å I = 100
  {002} 2θ = 24,9° d = 3,5 Å I = 90
- z neurejenostjo slabita
- {13l}, {20l} 2θ = 35 - 40°
  + {003} ⇒ dva trojčka ⇒ dobra urejenost
  ⇒ dva dubleta ⇒ slaba urejenost

- vzroki neurejenosti : V_{Al} v strukturi

Hinckleyev indeks kristaliničnosti

$$I = (h_1+h_2)/h$$

Slika