

Research on genesis of precious metals deposits in the Central Slovakian Neogene Volcanic Field

Peter Koděra

Recent related research projects

position: principal investigator

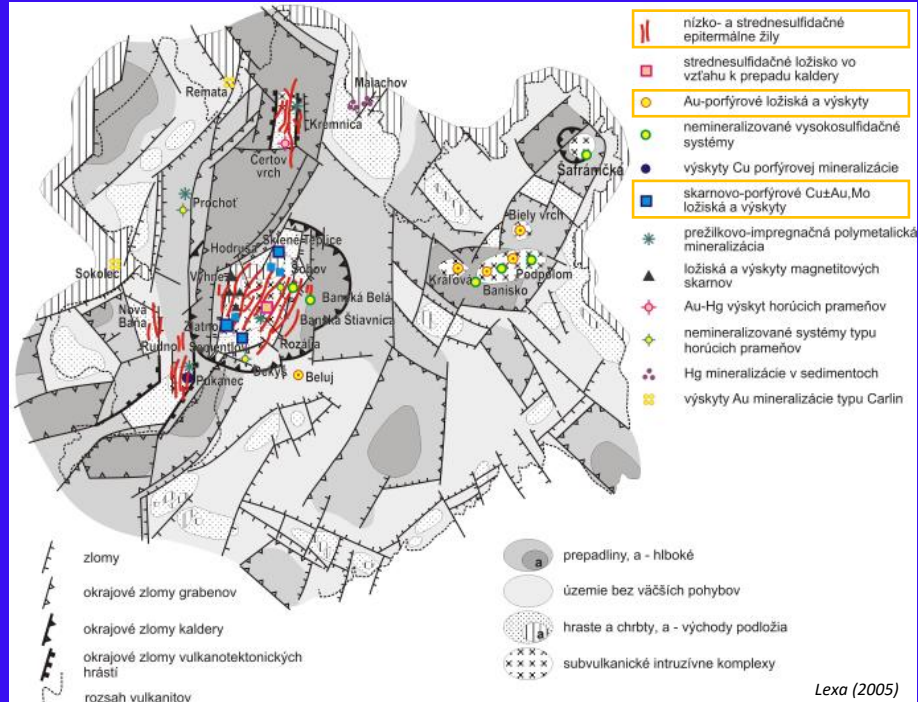
- **Genesis of precious metal epithermal and porphyry mineralisations in the stratovolcanoes Javorie and Štiavnica. VEGA grant, 2020 – 2023**
- **Complex model of base and precious metal mineralisation at the Rozália mine in Hodruša - Hámre. APVV grant, 2016 – 2020**
- **Mineralogy and genesis of economically important types of gold mineralisation in the Central Slovakian Neogene Volcanic Field. VEGA grant, 2015 - 2018**
- **Au-porphyry systems deposit models in the Central Slovakia Neogene Volcanic Field and environmental aspects of their exploitation. APVV grant, 2011 - 2014**

Precious metal deposits in the Central Slovakian Neogene Volcanic Field

- Main mineralised centers:

- *Štiavnica Stratovolcano* (mainly central zone)
- *Kremnické Vrchy Mts.* (mainly Kremnica horst)
- *Javorie Stratovolcano* (mainly central zone)

- Active exploration, mining, ore reserves

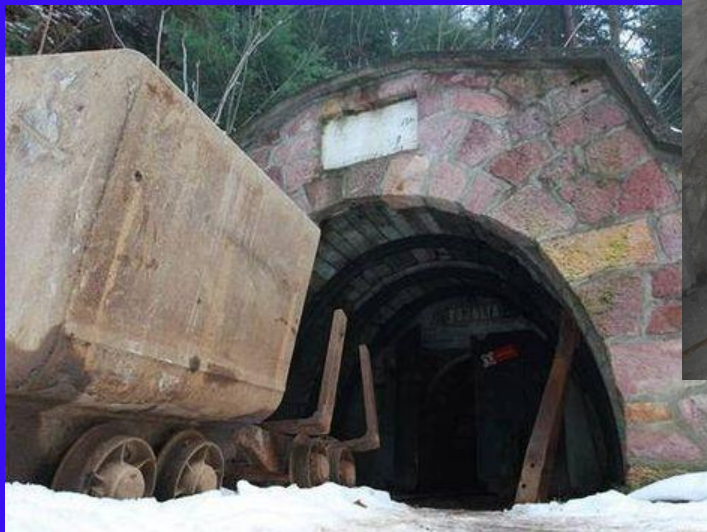


Lexa (2005)

Horst-graben structure

Complex model of base and precious metal mineralisation at the Rozália mine in Hodruša – Hámre

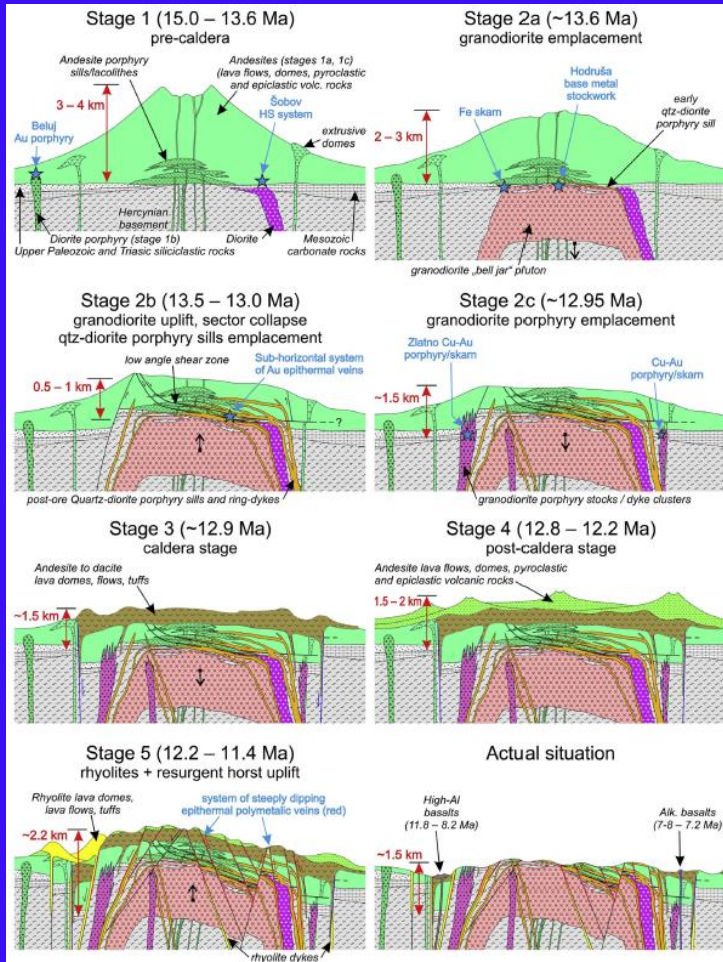
APVV grant, 2016 – 2020



Outcomes of the project

- Structural-geological model of the deposit:
 - *Model of the central zone of the Štiavnica stratovolcano*
 - *Model of the magmatic evolution of the Štiavnica stratovolcano*
- Model of mineralisation at the deposit
- **Model of hydrothermal alteration at the deposit**
- **Genetic model of the deposit**
- Criteria for ore prognosis (regional, local)
- Modelling of the deposit in GIS
 - *Complex structured spatial database*
 - *3D model of mine works*
 - *3D model of geology of the deposit*
 - *3D model of distribution of Au-Ag at the deposit*

Magmatic evolution in the Štiavnica stratovolcano (Rottier et al., 2020)



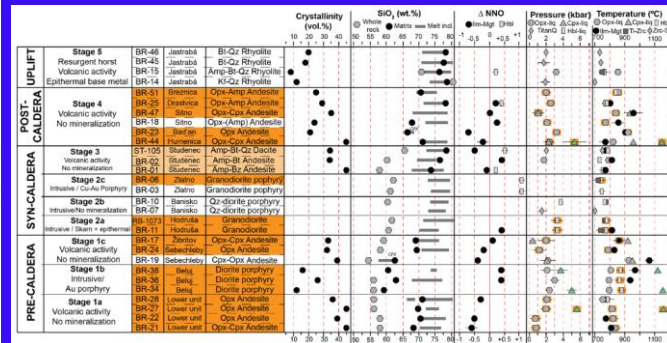
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Journal of Volcanology and Geothermal Research

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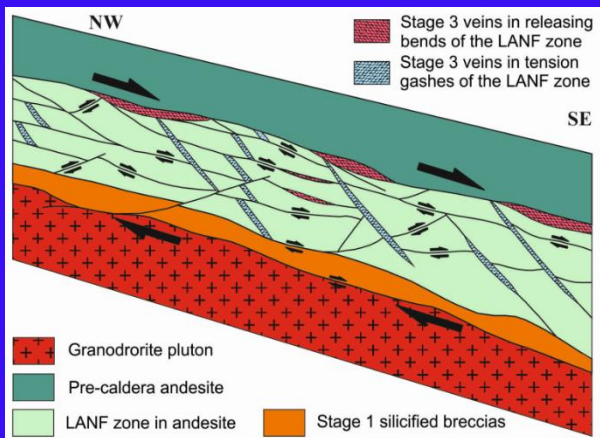
Magmatic evolution of the mineralized Štiavnica volcano (Central Slovakia): Evidence from thermobarometry, melt inclusions, and sulfide inclusions

Bertrand Rottier^{a,b,c,*}, Andreas Audéat^d, Peter Koděra^d, Jaroslav Lexa^e



- **SHRIMP U-Pb dating** of associated intrusive and volcanic rocks
- the deposits were formed during periods of **upper crustal reservoir** cooling when the residual melt has reached fluid saturation

Mineralogical model of the deposit (Kubač et al., 2018)



Mineralogy and Petrology (2018) 112:705–731
<https://doi.org/10.1007/s00710-018-0558-y>

ORIGINAL PAPER



Mineralogy of the epithermal precious and base metal deposit Banská Hodruša at the Rozália Mine (Slovakia)

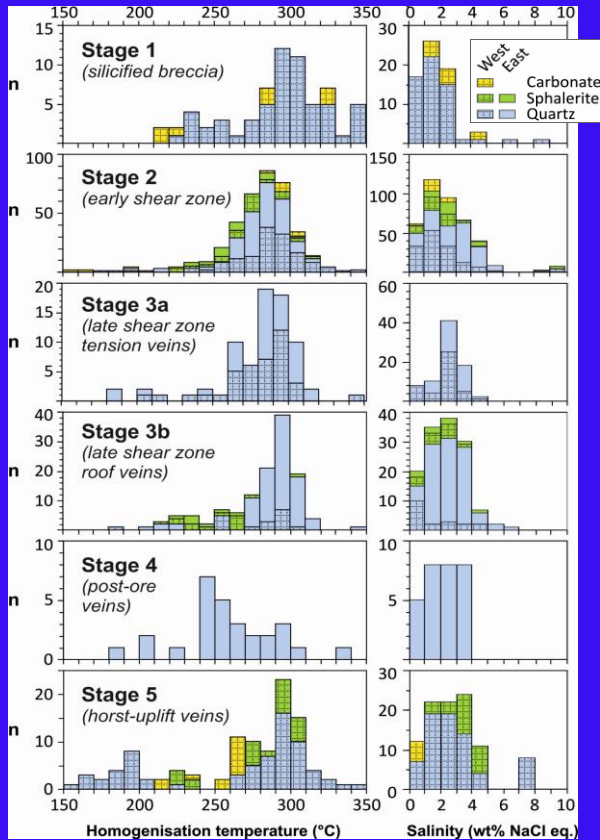
Alexander Kubač¹ · Martin Chovan² · Peter Koděra³ · J. Richard Kyle³ · Peter Žitňan⁴ · Jaroslav Lexa⁵ · Rastislav Vojtko⁶

- The ore is hosted by a **shear zone**
- **Paragenetic charts:** 3 types of epithermal ore veins, different structural setting and mineralogy with 3 stages of evolution

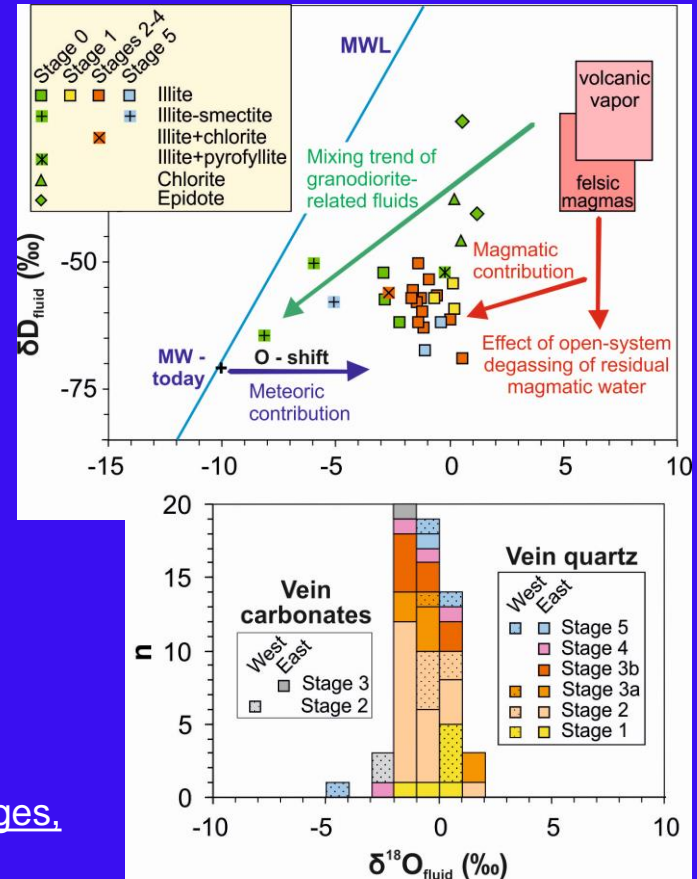
Tectonic event	Early development of shear zone			Late development of shear zone		Horst uplift
Stage	1	2		3	4	
Vein system	Svetozár	Karolína		Krištof	Agnesa	Post-ore veins
Assemblage		2A	2B	3A	3B	Horst-related
Quartz	—	—	—	—	—	—
Rhodonite	—	—	—	—	—	—
Rhodochrosite	—	—	—	—	—	—
Chlorite	—	—	—	—	—	—
Calcite	—	—	—	—	—	—
Dolomite (Fe)	—	—	—	—	—	—
Siderite	—	—	—	—	—	—
Adularia	—	—	—	—	—	—
Illite	—	—	—	—	—	—
Hematite	—	—	—	—	—	—
Pyrite	—	—	—	—	—	—
Sphalerite	—	—	—	—	—	—
Galenite	—	—	—	—	—	—
Chalcopryrite	—	—	—	—	—	—
Gold	—	—	—	—	—	—
Hessite	—	—	—	—	—	—
Petzite	—	—	—	—	—	—
Te-polybasite	—	—	—	—	—	—
Cu-cervelleite	—	—	—	—	—	—
Cu-Pb-Bi sulphosalts	—	—	—	—	—	—
Polybasite-Pearceite	—	—	—	—	—	—
Ag-Bi sulphosalts	—	—	—	—	—	—
Cervelleite	—	—	—	—	—	—
Acanthite	—	—	—	—	—	—

Tektonická udalosť	Relatívny pokles centrálného bloku	Vývoj střížnej zóny			Výzdvih hrásti
Etapa vývoja	IV	V			VII
Štádium	-	1 (qtz-rd)	2 (sulf-Au)	3 (qtz)	-
Žilný typ	silicit	Karolína	Karolína Krištof Agnesa	Pomimeralizačné žily	Hrástové žily
Kremeň	—	—	—	—	—
Rodonit	—	—	—	—	—
Kutnohorit	—	—	—	—	—
Rhodochrozit	—	—	—	—	—
Chlorit	—	—	—	—	—
Kalcit	—	—	—	—	—
Dolomit (Fe)	—	—	—	—	—
Siderit	—	—	—	—	—
Adularia	—	—	—	—	—
Illit	—	—	—	—	—
Hematit	—	—	—	—	—
Epidot	—	—	—	—	—
Pyrit	—	—	—	—	—
Sfalerit	—	—	—	—	—
Galenit	—	—	—	—	—
Chalkopryrit	—	—	—	—	—
Zlato/elektum	—	—	—	—	—
Hessit	—	—	—	—	—
Petzit	—	—	—	—	—
Alit	—	—	—	—	—
Tetraedrit	—	—	—	—	—
Tennantit	—	—	—	—	—
Polybázit	—	—	—	—	—
Pearceit	—	—	—	—	—
(Cu)-Cervelleit	—	—	—	—	—
Ag-Cu-Bi sulfosoli	—	—	—	—	—
Akanit	—	—	—	—	—

Properties of paleofluids at the Rozália mine

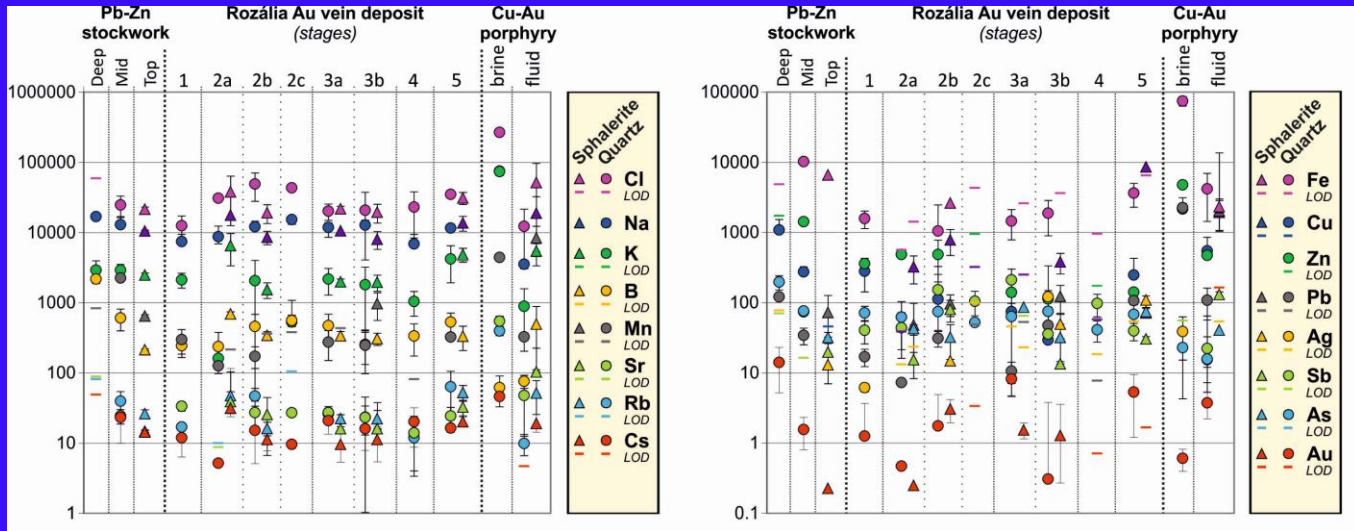


homogeneous $\delta^{18}\text{O}_{\text{fluid}}$ of magmatic origin

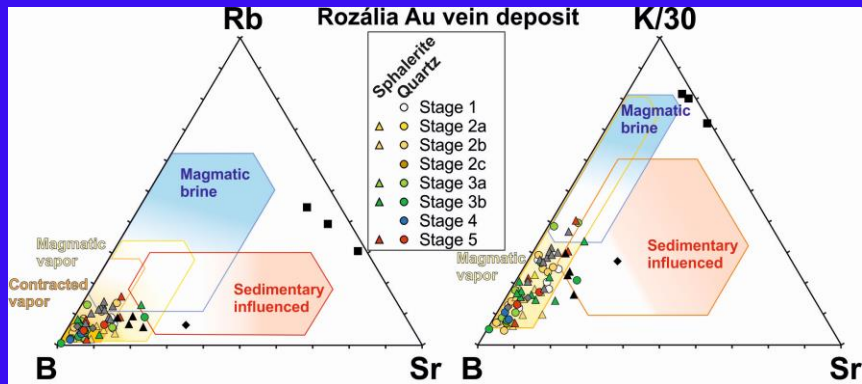


No apparent differences between stages,
neither W and E parts of the deposit

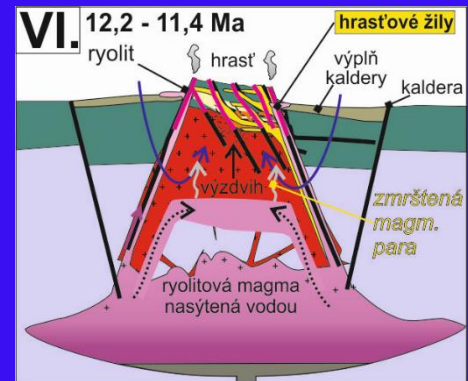
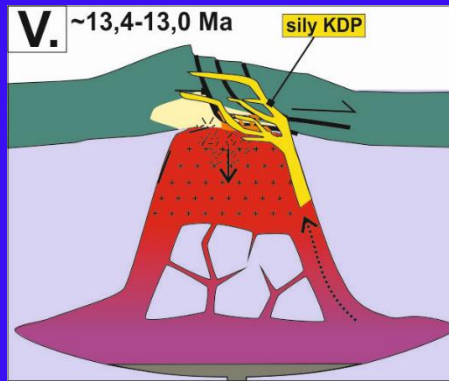
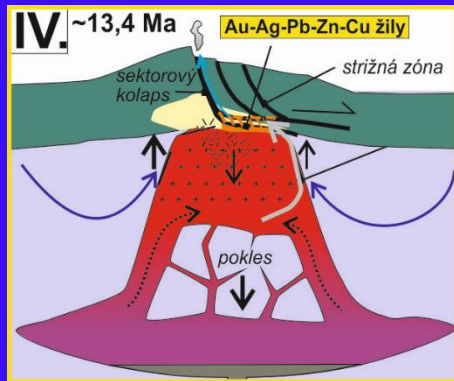
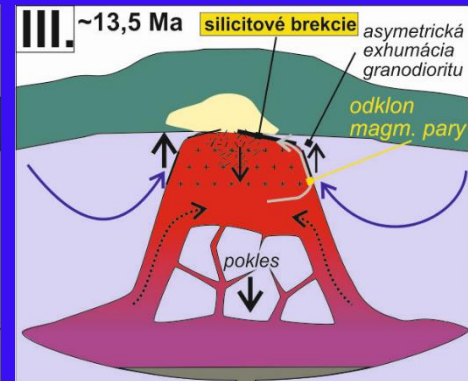
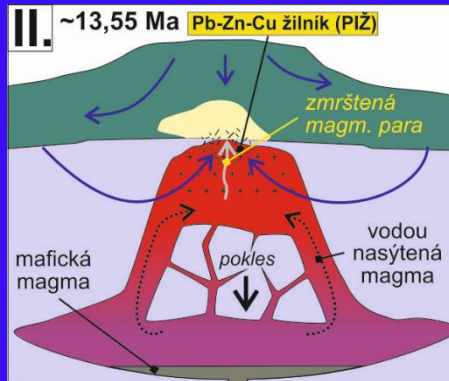
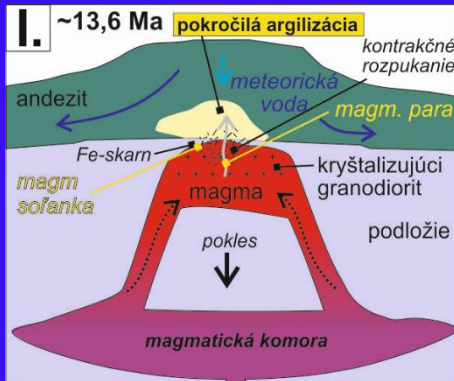
Properties of paleofluids at the Rozália mine (LA ICPMS)



- All deposits and stages have similar composition and **increased B, As, Sb, Cs**
- **Magmatic vapor** exsolved from evolved interstitial melt and **contracted to liquid** during ascent from magma reservoir
- Accumulated fluid was liberated during **periodical tectonic events**

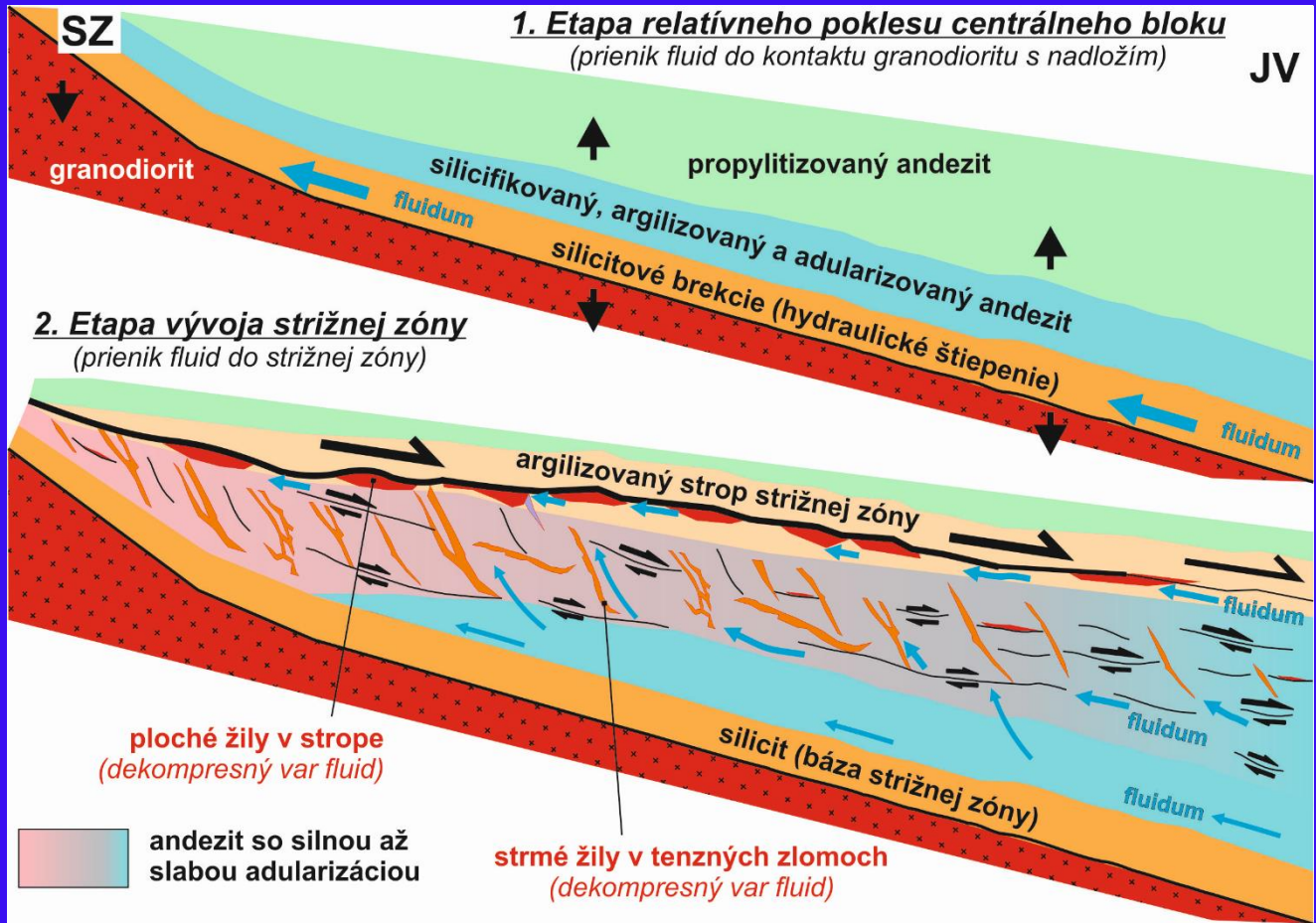


Model of magmatic-hydrothermal evolution of mineralisations at the Rozália mine

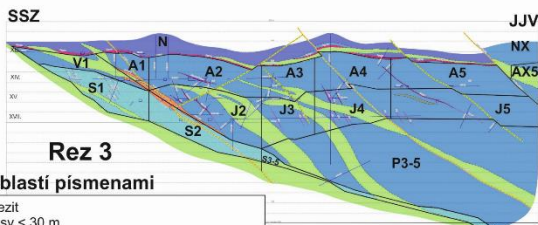
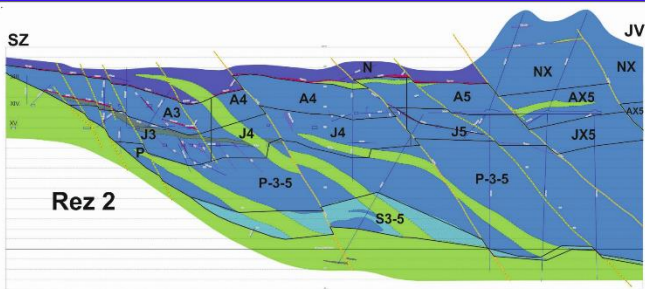


- Au-Ag at Rozália mine is related to **quick uplift of granodiorite and sector collapse of stratovolcano**

Model of shear zone evolution and fluid flow



Distribution of zones and vein types in shear zone – eastern deposit



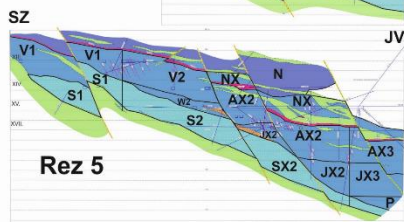
Kódovanie oblastí písmenami

N - nadložný andezit
 A - podložie Agnesy < 30 m
 V - oblasť žil Viktor (v podloží Karolíny), < 30 m pod Agnesou
 J - oblasť žil Ján (> 30 m pod Agnesou)
 P - podložný andezit (> 60 m pod Agnesou)
 S - silicity
 X - oblasť ložiska, kde nadložný andezit je čiastočne argilizovaný

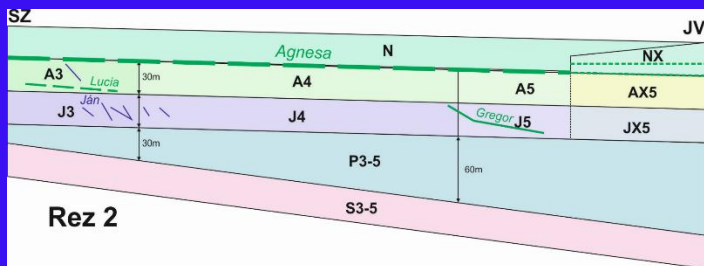
Kódovanie oblastí číslami

oblasti, kde vzdialenosť medzi Agnesou a silicity je:
 1 - < 30 m
 2 - 30 - 60 m
 3 - 60 - 90 m
 4 - 90 - 120 m
 5 - 120 - 150 m

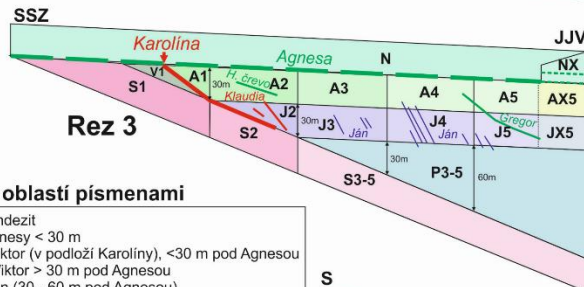
Rez 4



Rez 5



Rez 2



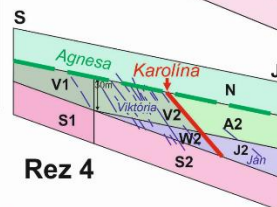
Rez 3

Kódovanie oblastí písmenami

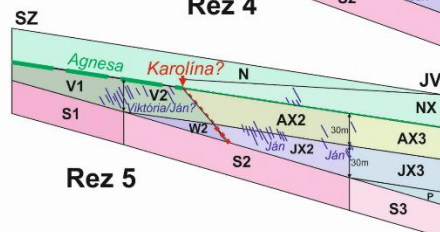
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Rez 4

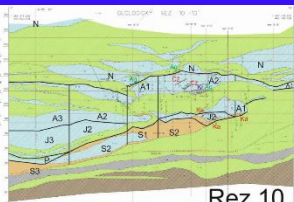


Rez 5

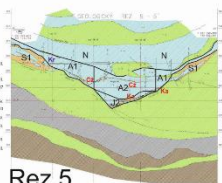
Distribution of zones and vein types in shear zone – western deposit

Kódovanie podľa vzdialenosti obzoru od stropu strižnej zóny

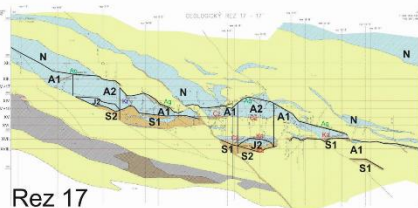
N - nadložný andezit
A - < 30 m (so žilami Agnesa)
J - 30 - 60 m (do žilami Ján/Krištof)
P - > 60 m („podložný“ andezit)
S - silicity



Rez 10



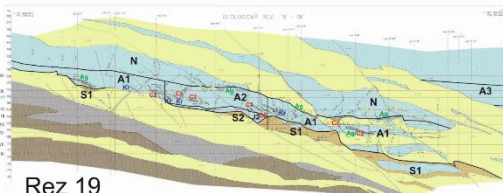
Rez 5



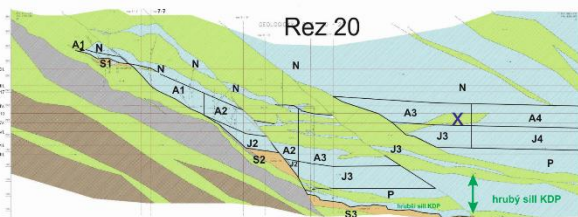
Rez 17

Kódovanie podľa rozpätia strižnej zóny

celková vzdialenosť medzi stropom a silicityom je:
1 - < 30 m
2 - 30 - 60 m
3 - 60 - 90 m
4 - 90 - 120 m



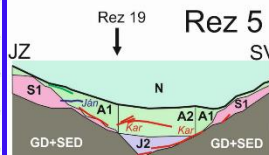
Rez 19



Rez 20

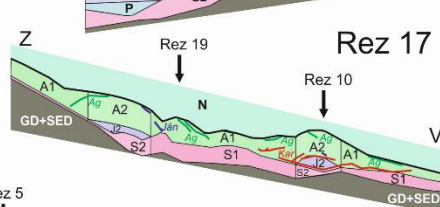
Kódovanie podľa vzdialenosti obzoru od stropu strižnej zóny

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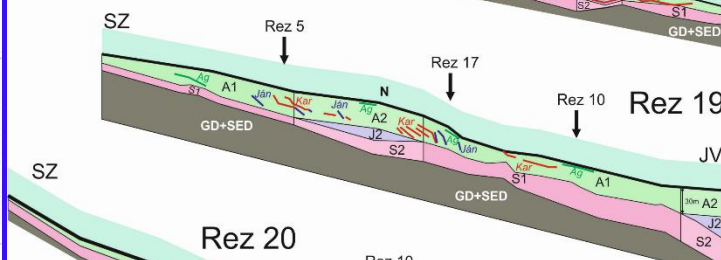


Rez 19

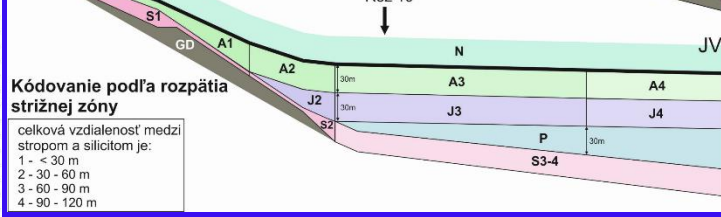
Rez 5



Rez 17



Rez 10



Rez 20

Kódovanie podľa rozpätia strižnej zóny

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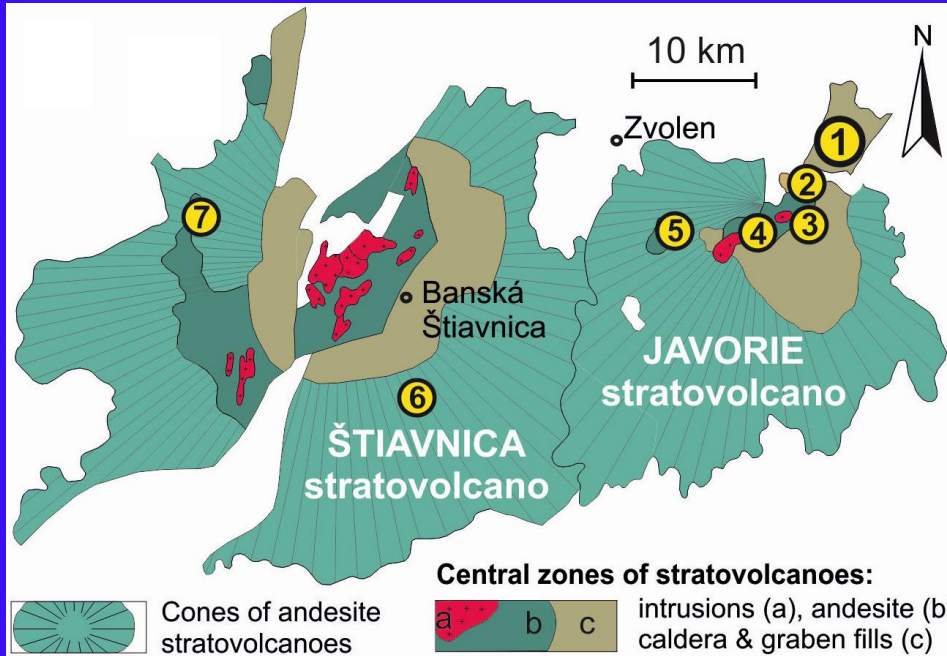
Genéza zlata v Au-porfýrových systémoch

APVV (2010-2015), VEGA (2008-2021)

80 ton zlata



Au-porphyry systems in the Central Slovakian Neogene Volcanic Field



Deposit

1 – Biely Vrch

Occurrences

2 – Podpolom

3 – Slatinské lazy

4 – Banisko

5 – Kráľová

6 – Beluj

7 – Župkov

- Centered on small **diorite** porphyry stocks
- **Biely Vrch** - **biggest** and best explored
- **Exceptionally low Cu/Au ratio**

Locality	Resources (Mt)	Au (ppm)	Cu (ppm)	Cu/Au
Biely vrch	140	0.57	178	176
Kráľová	47.8	0.29	456	813
Slat. Lazy	12.5	0.3	243	360
Beluj	58.4	0.2-0.4	250	578

Genesis of the porphyry Au deposit Biely Vrch

- Gold mineralization formed from nearly **anhydrous Fe-K-Na-Cl salt melt**, coexisting with **hydrous vapor of very low density**

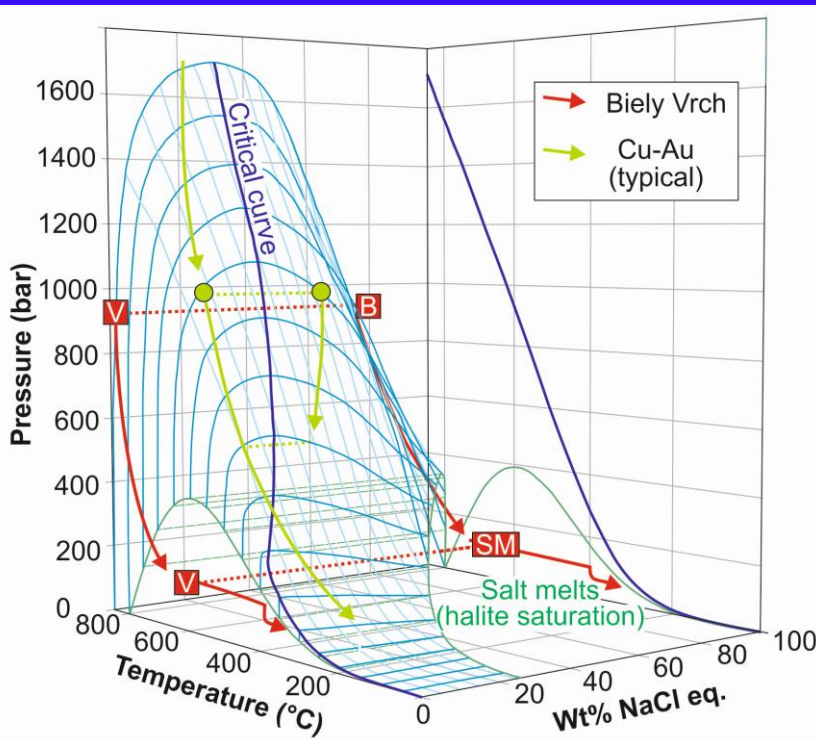
Magmatic salt melt and vapor: Extreme fluids forming porphyry gold deposits in shallow subvolcanic settings

Peter Koděra¹, Christoph A. Heinrich², Markus Wälle², and Jaroslav Lexa²

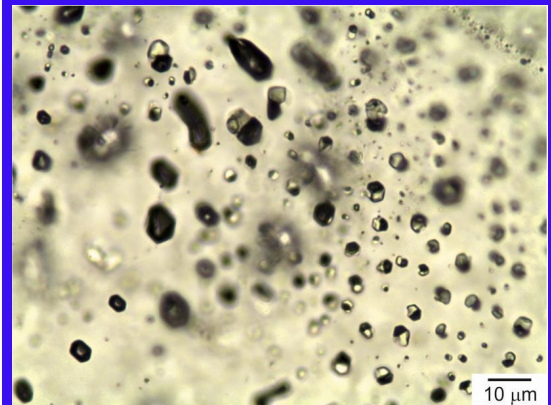
¹Department of Geology of Mineral Deposits, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia

²GEOLOGY, June 2014; v. 42; no. 6; p. 495–498; Data Repository item 2014177 | doi:10.1130/G35270.1 | Published online 10 April 2014

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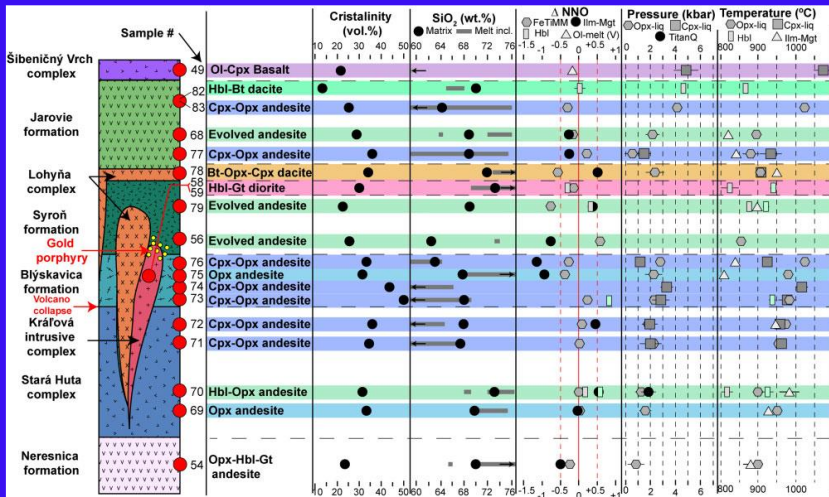


- Low depth of emplacement of magma → low density of vapor (and sulfur fugacity) prevented transport of Au and crystallisation of Cu sulfides



Magmatic evolution in the Javorie stratovolcano

(Rottier et al., 2019)



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PETROLOGY

Journal of Petrology, 2019, Vol. 60, No. 12, 2449–2482

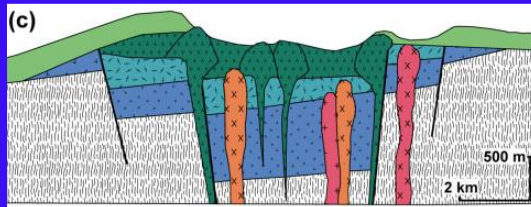
doi: 10.1093/petrology/egz014

Advance Access Publication Date: 11 March 2020

Original Article

Origin and Evolution of Magmas in the Porphyry Au-mineralized Javorie Volcano (Central Slovakia): Evidence from Thermobarometry, Melt Inclusions and Sulfide Inclusions

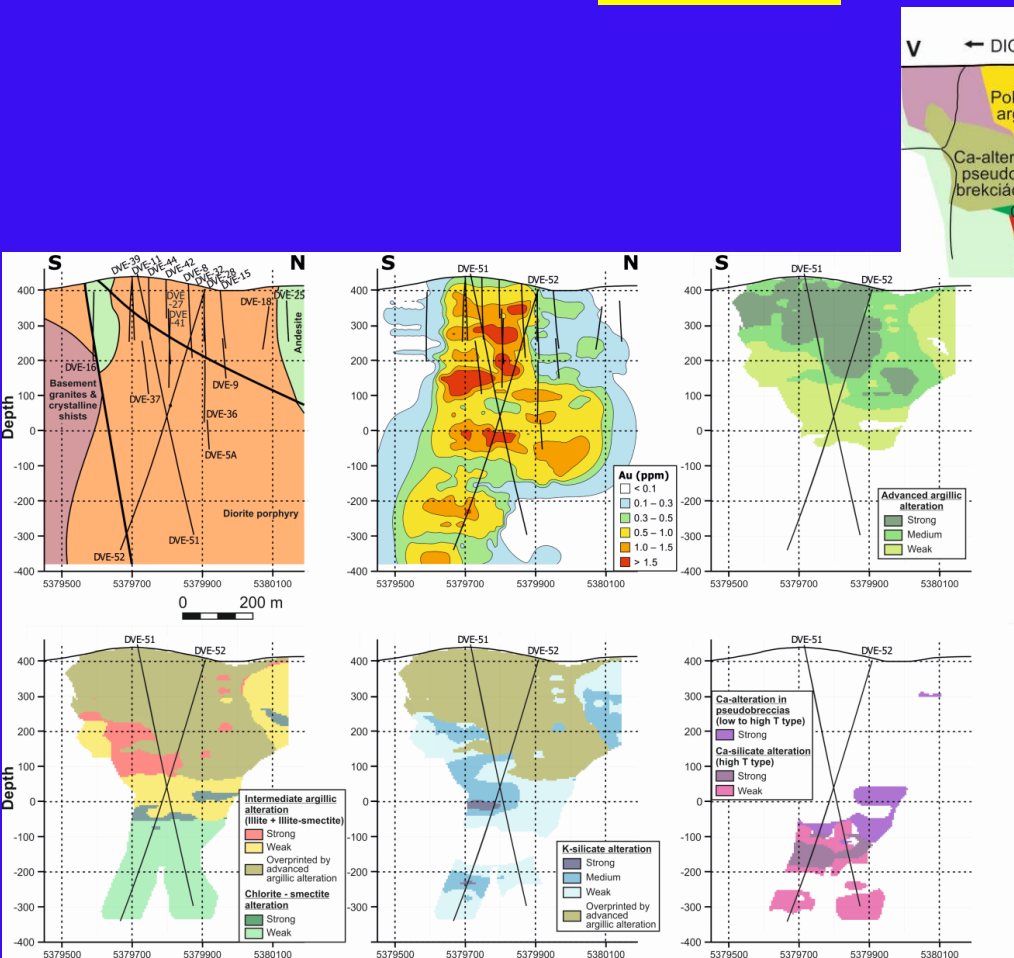
Bertrand Rottier^{1,2,3,*}, Andreas Audétat¹, Peter Kodera⁴ and Jaroslav Lexa⁵



- two levels of magma chambers, sulfide saturated during entire evolution
- **Cu/Au ratios** in magmatic sulfides and predicted in exsolved fluids are up to 100 times higher than in porphyry deposits → **extremely low Cu/Au ratios acquired during hydrothermal stage**
- recent SHRIMP U-Pb dating of the Biely Vrch intrusion (13.53 ± 0.15 Ma)

Hydrothermal alteration & Au distribution - Biely vrch deposit

3D models



- criteria for the 3D GIS alteration model → correlation of mineral and chemical composition of rocks

Gold in Au-porphyry systems

Mineralium Deposita
https://doi.org/10.1007/s00126-018-0798-0

ARTICLE

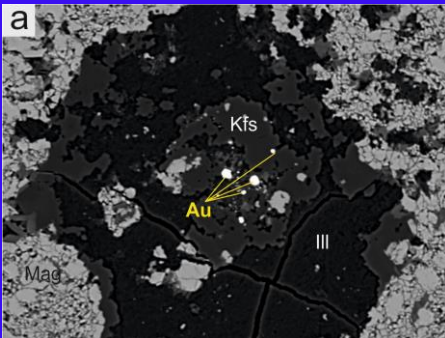
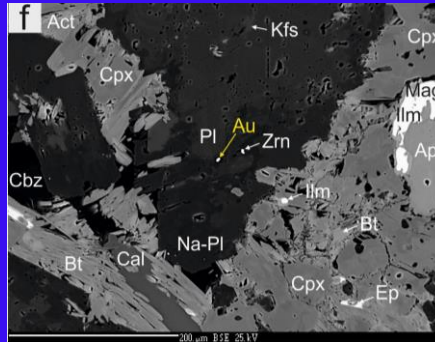


Distribution and composition of gold in porphyry gold systems: example from the Biely Vrch deposit, Slovakia

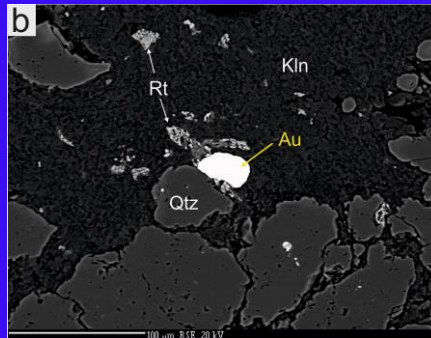
Peter Kodéra¹ · Jaroslav Kozák¹ · Jana Brčková¹ · Martin Chovan² · Jaroslav Lexa³ · Michal Jánošík¹ · Adrián Biroň⁴ · Peter Uhlík¹ · František Bakos⁵

Typical mineral paragenesis

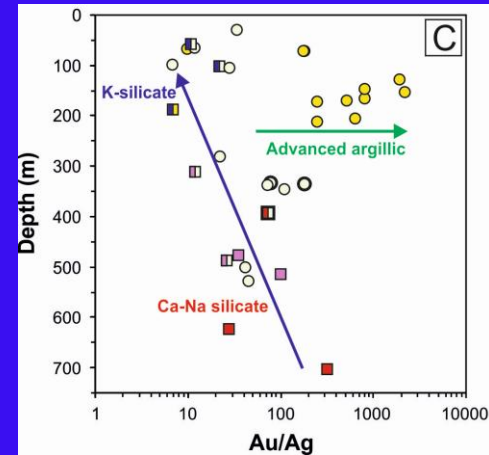
Primary in high T alteration
→



Residual in intermediate alteration



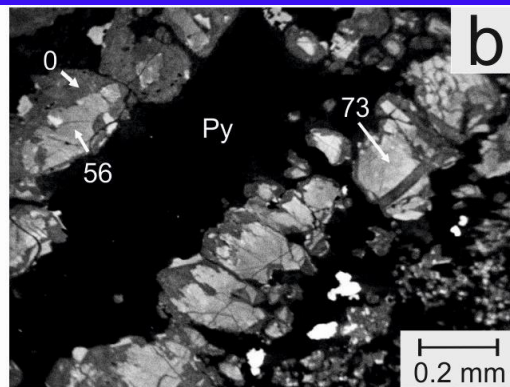
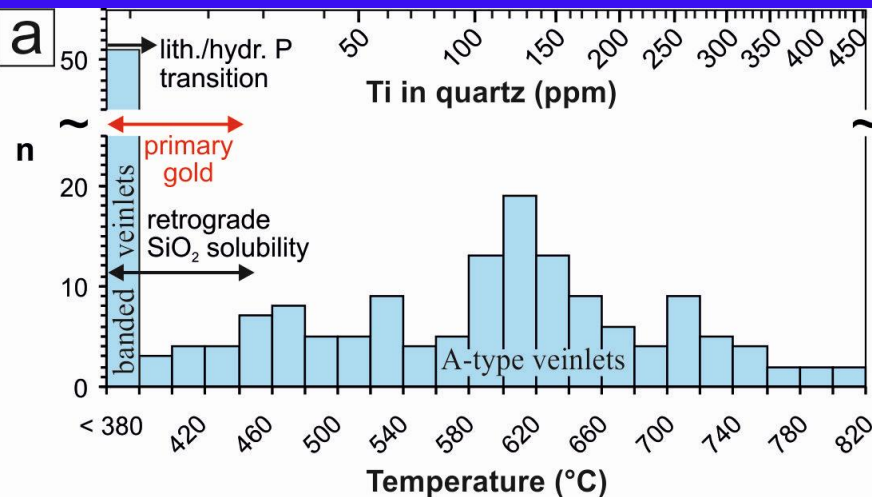
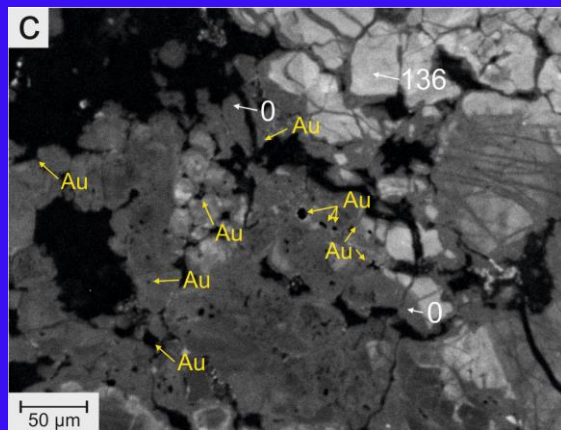
Remobilised in advanced argillic alteration



- *Decrease in fineness towards surface* → cooling of ascending fluids
- *Increase in gold fineness in advanced argillic alteration* → partial remobilisation at low pH

Temperature of gold precipitation

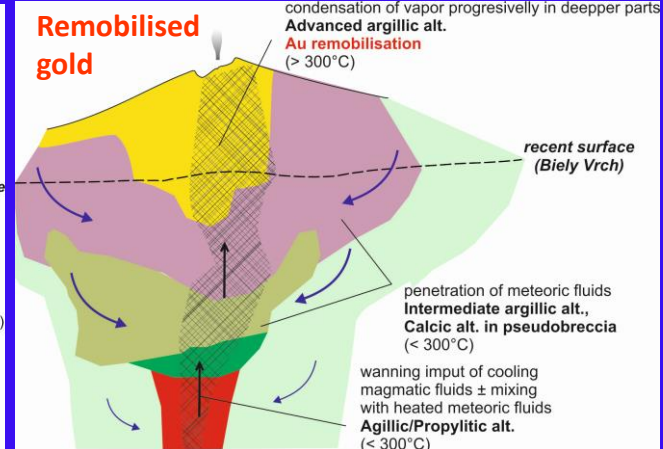
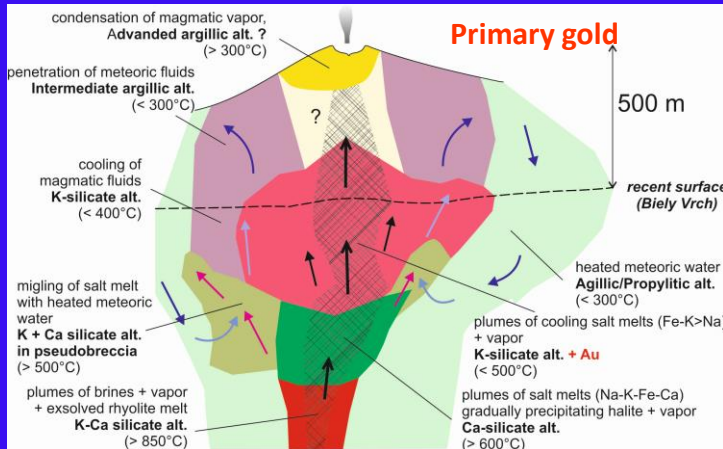
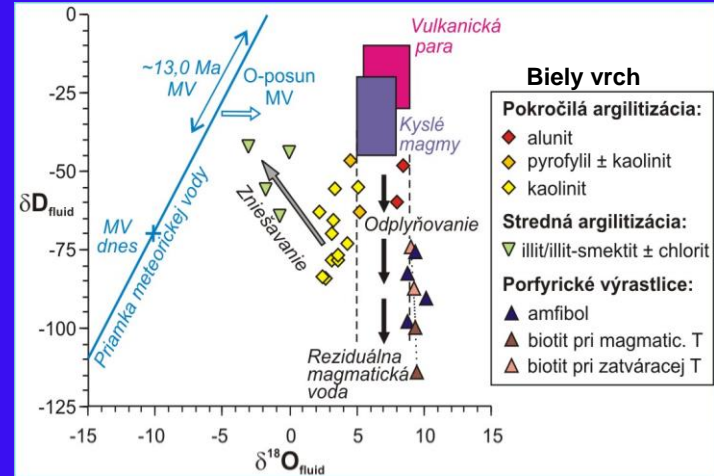
- **Predominance of gold in altered rock rather than vein quartz** can be explained by **retrograde solubility of quartz** during isobaric cooling from **~450° to 375°C** at low pressure (Fournier, 1985)
- Rare precipitation of **primary gold in vein quartz** occurred at **<380°C** as indicated by the **low Ti content** (<8 ppm) of the quartz



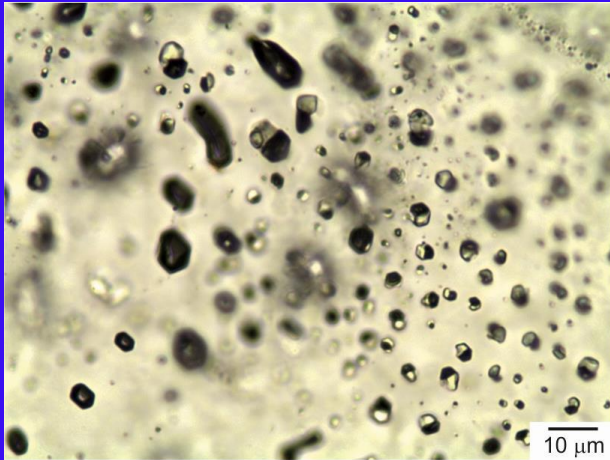
TitaniQ geothermometry
(Thomas et al., 2010)

Genetic model of Au-porphyry systems

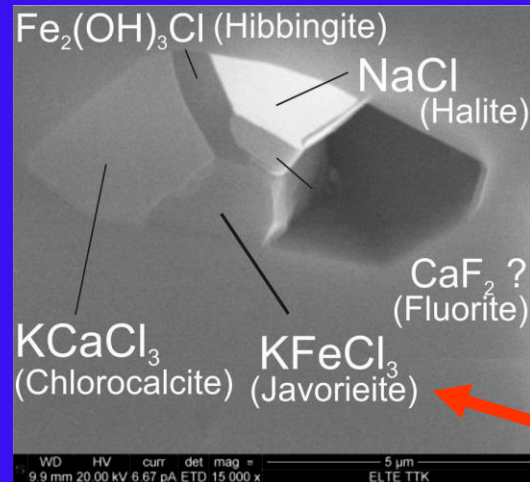
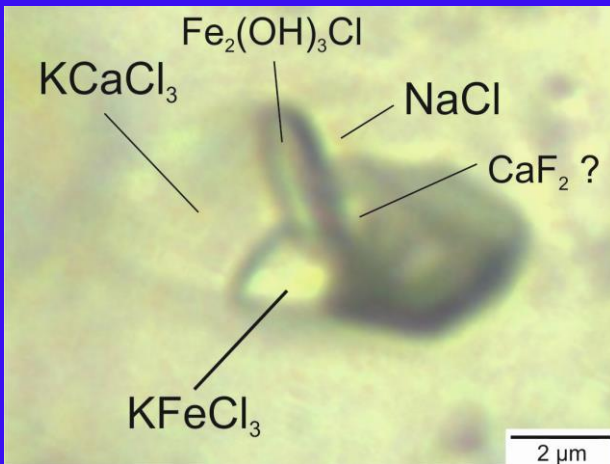
- Synthesis of geological and microanalytical data and 3D models of alteration and mineralisation
- Fluid sources – mostly magmatic (vapor and salt melts), intermediate argillic mostly meteoric



Paleofluids

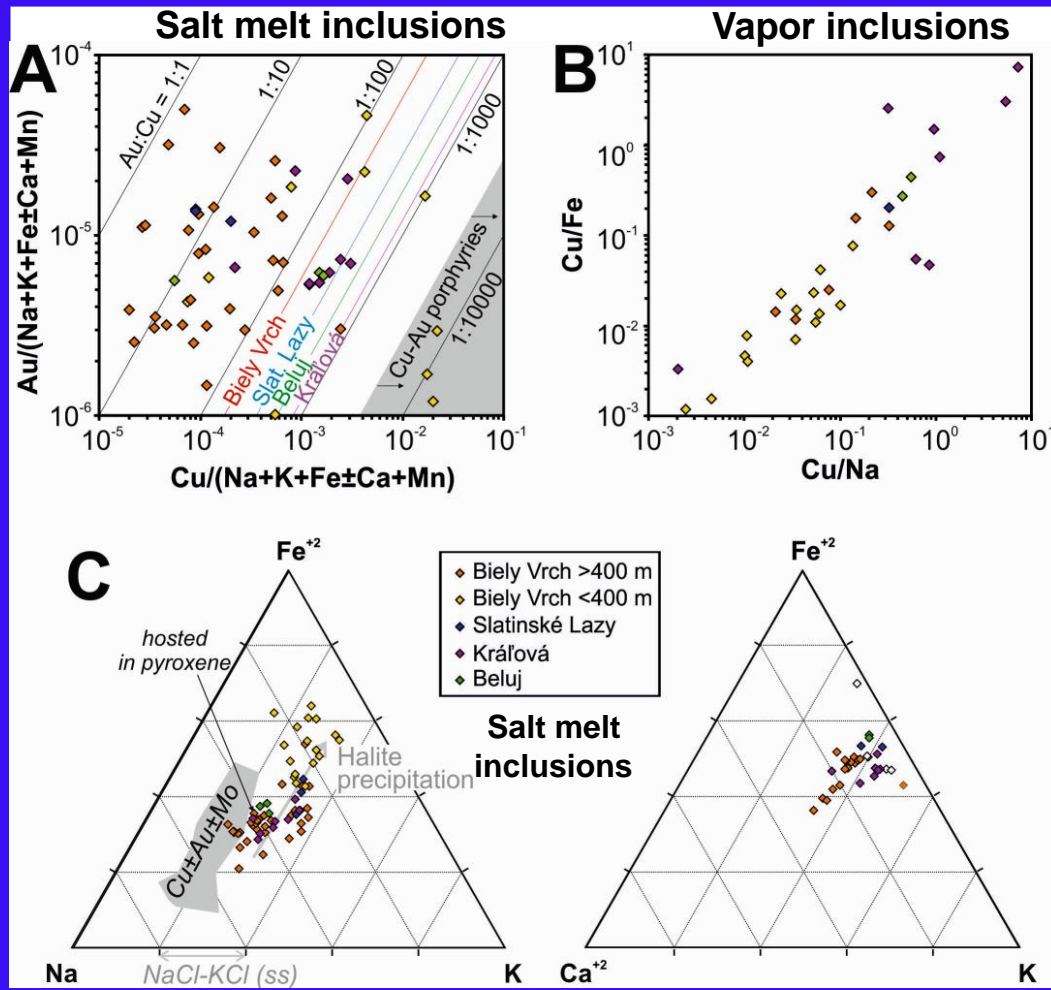


- Fluid inclusions in vein quartz (all localities):
 - **Vapor** (most common)
 - **Crystallised salt melts** (mainly in A-type veins, $T_h > 600^\circ\text{C}$)
 - **Aqueous solutions** (rare, secondary, also in calcite) – related to low-temperature alteration



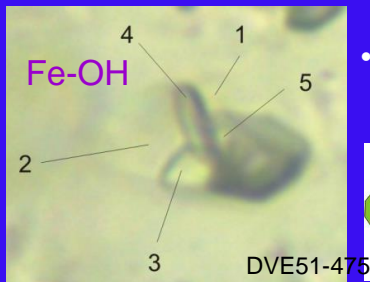
**A NEW
MINERAL**

Composition of paleofluids – LA ICPMS data



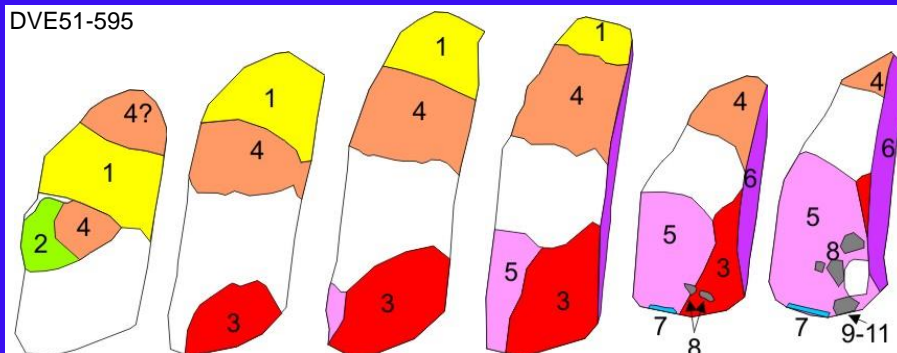
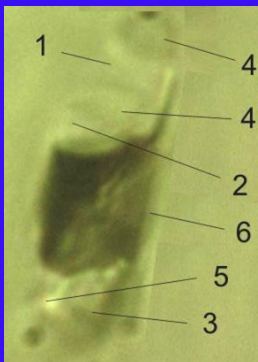
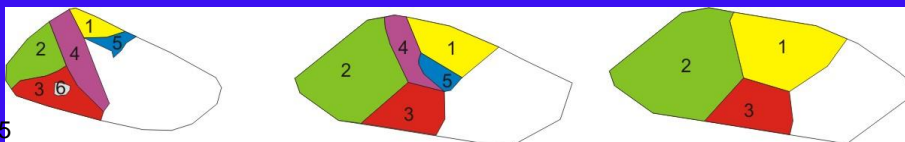
- Salt melts have tens ppm Au and Cu/Au ratio is lower than in ore
- Deepest parts of B. Vrch (> 400 m) and on other localities the **composition of salt melts is close to Cu-Au-Mo porphyries**
- In shallow parts of B. Vrch (< 400 m) salt melts have **higher content of Fe on the extent of Na**
- Vapor inclusions - increased Cu, (xx – xxx ppm Cu), but **without Au and S** → low fS_2 prevented sulfide

Combined Raman and FIB-SEM-EDX-EBSD-SAED analyses of salt melt inclusions



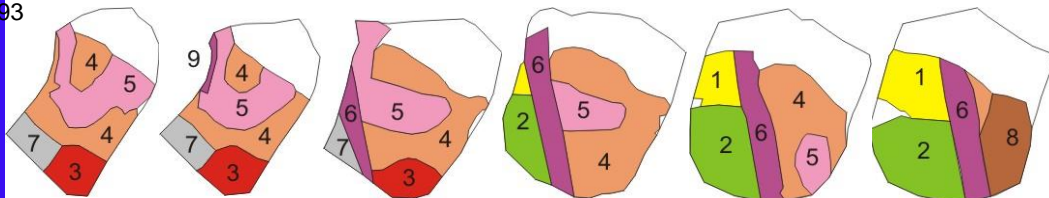
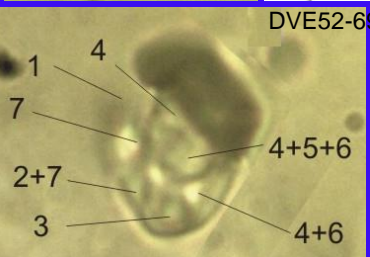
- Phases with the characteristic Raman spectra were exposed to the surface in vacuum by FIB technique

4 - Fe-OH phase



6 - Fe-OH phase

6 - Fe-OH phase



1 – NaCl, 2 – KCaCl₃, 3 – KFeCl₃, 4 – NaK₃FeCl₆, 5 – K₂FeCl₄

Daughter minerals in salt melt inclusions

Eur. J. Mineral.
2017, 29, 995–1004
Published online 22 September 2017

Javorite, KFeCl_3 : a new mineral hosted by salt melt inclusions in porphyry gold systems

PETER KODĚRA^{1,*}, ÁGNES TAKÁCS², MARTIN RACEK³, FRANTIŠEK ŠIMKO⁴, JARMILA LUPTÁKOVÁ⁵, TAMÁS VÁCZI^{2,6} and PETER ANTAL⁷



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Identification of anhydrous CaCl_2 and KCaCl_3 in natural inclusions by Raman spectroscopy

Svetlana Grishina^a, Peter Koděra^{b,*}, Lucas M. Uriarte^{c,d}, Jean Dubessy^d, Aleksandr Oreshonkov^{e,f}, Sergey Goryainov^g, František Šimko^h, Igor Yakovlev^h, Evgenii M. Roginskii^h

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DOI: 10.1002/jms.4605

RESEARCH ARTICLE

Journal of
RAMAN
SPECTROSCOPY WILEY

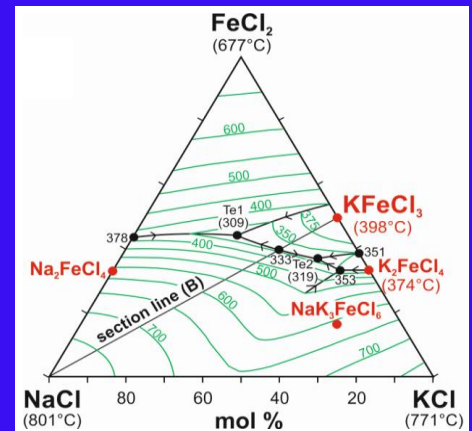
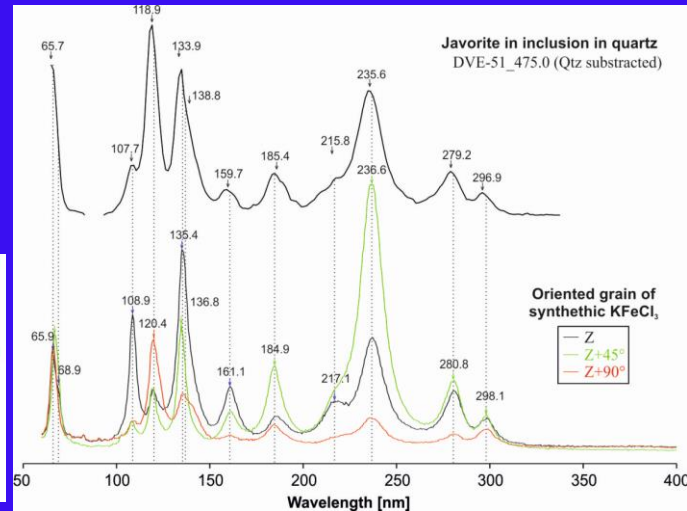


Application of Raman spectroscopy for identification of rinneite ($\text{K}_3\text{NaFeCl}_6$) in inclusions in minerals

Svetlana Grishina¹ | Peter Koděra² | Sergey Goryainov¹ |
Aleksandr Oreshonkov^{3,4} | Yuri Seryotkin^{1,5} | František Šimko⁶ |
Alexander G. Polozov⁷

Ferrous hydroxychlorides hibbingite ($\gamma\text{-Fe}_2(\text{OH})_3\text{Cl}$) and parahibbingite ($\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$) as a concealed sink of Cl and H_2O in ultrabasic and granitic systems

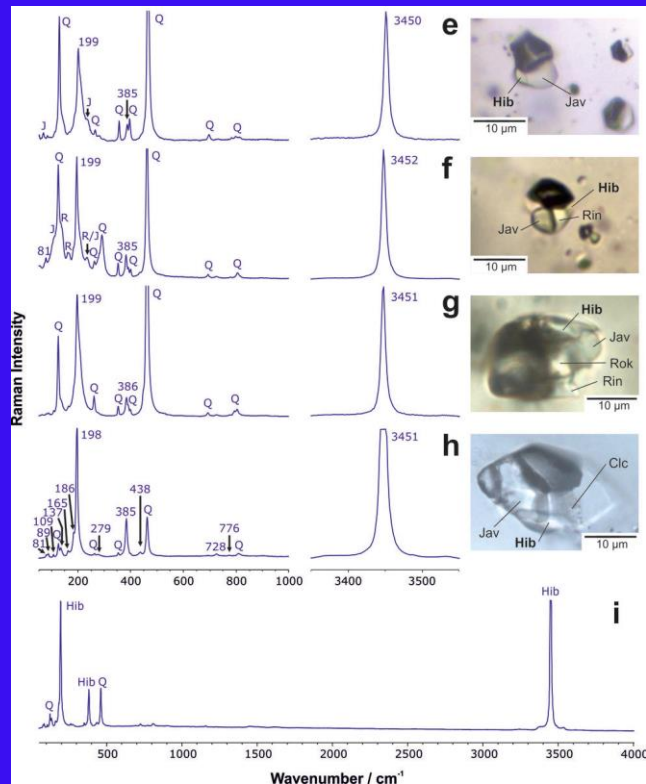
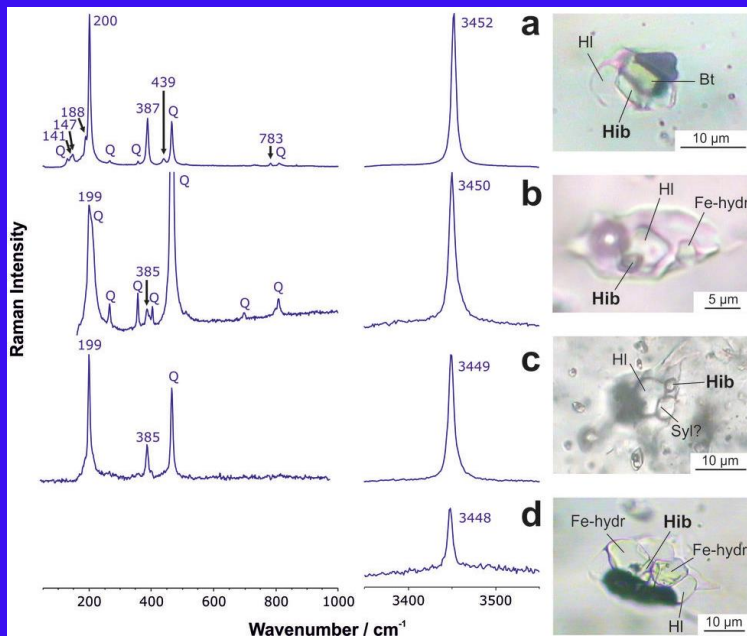
Peter Koděra, Juraj Majzlan, Kilian Pollok, Stefan Kiefer, František Šimko, Eva Scholtzová, Jarmila Luptáková, and Grant Cawthorn



American Mineralogist

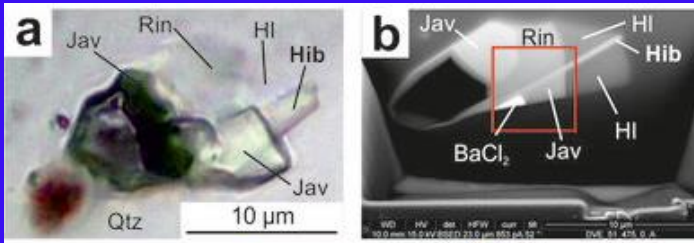
Hibbingite $\gamma\text{-Fe}_2(\text{OH})_3\text{Cl}$ in inclusions

- Hibbingite described from altered mafic intrusives, but not identified in inclusions yet

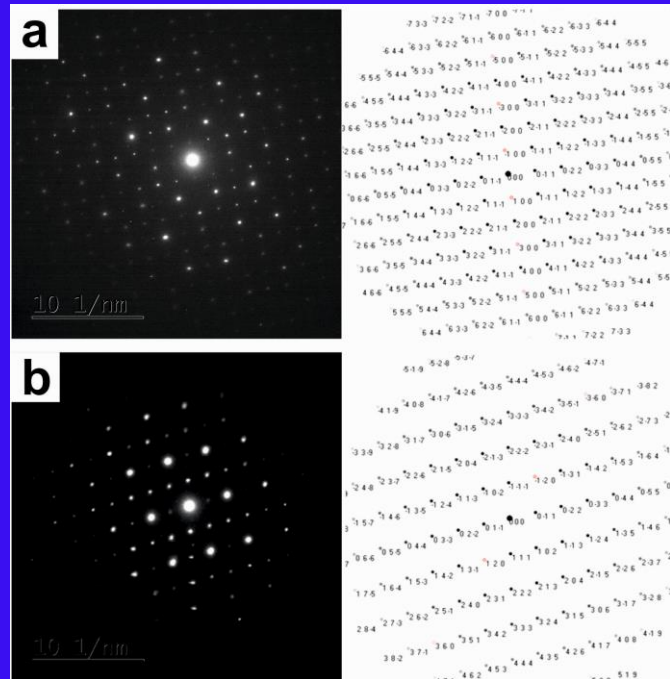
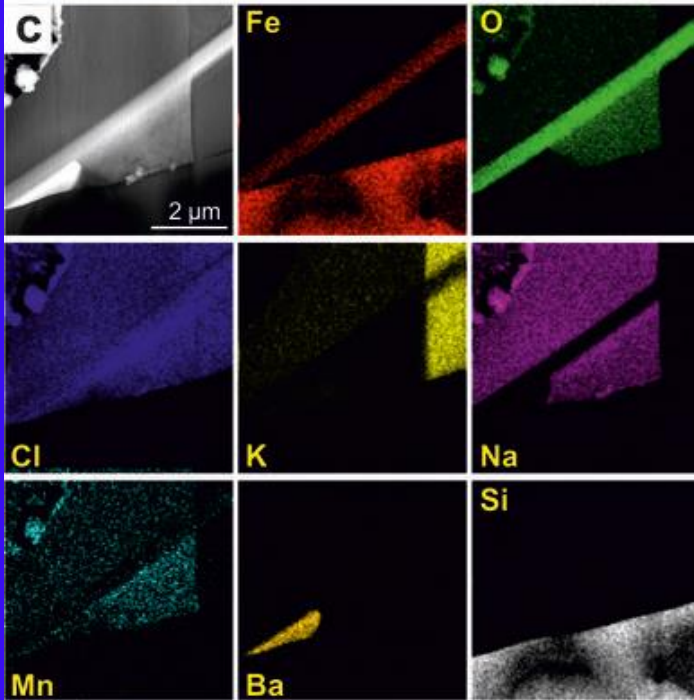


- Distinct Raman spectrum of the mineral – not published yet
- In salt melt inclusion it is the only phase which stores water (OH group)

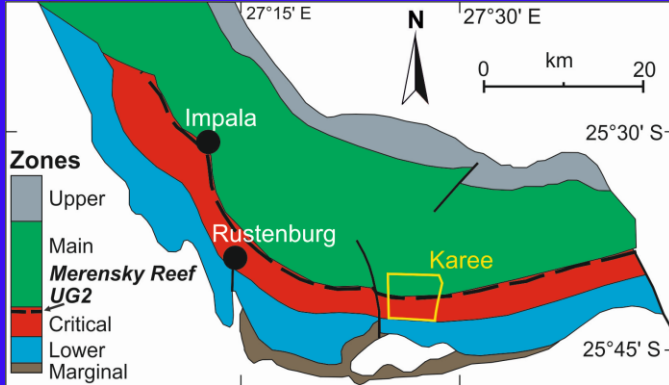
Hibbingite $\gamma\text{-Fe}_2(\text{OH})_3\text{Cl}$ in inclusions



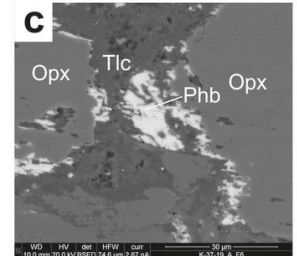
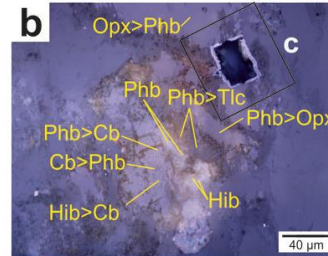
- Hibbingite identified by combination of Raman and FIB-SEM-TEM (TEM-EDX and TEM-SAED)



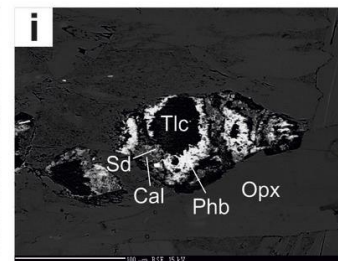
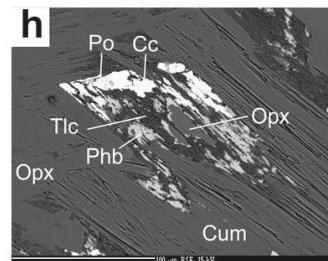
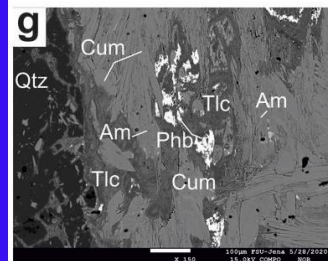
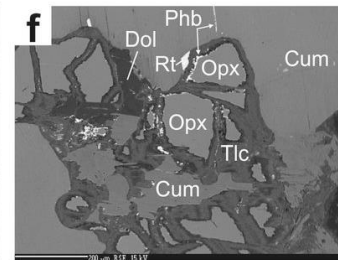
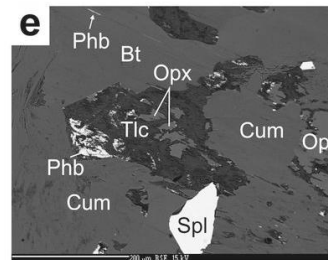
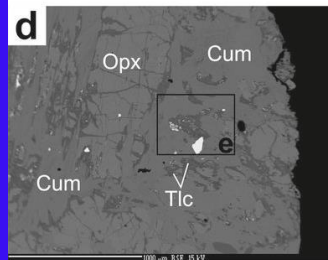
Parahibbingite $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ – a new mineral



- Parahibbingite found in pyroxenite from the Karee Pt mine in Bushveld Complex, South Africa

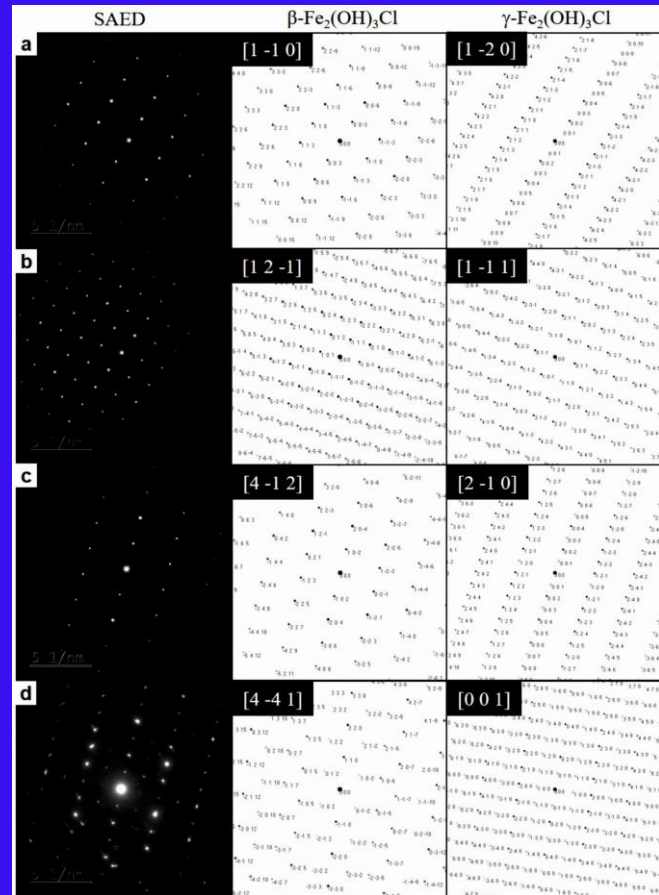
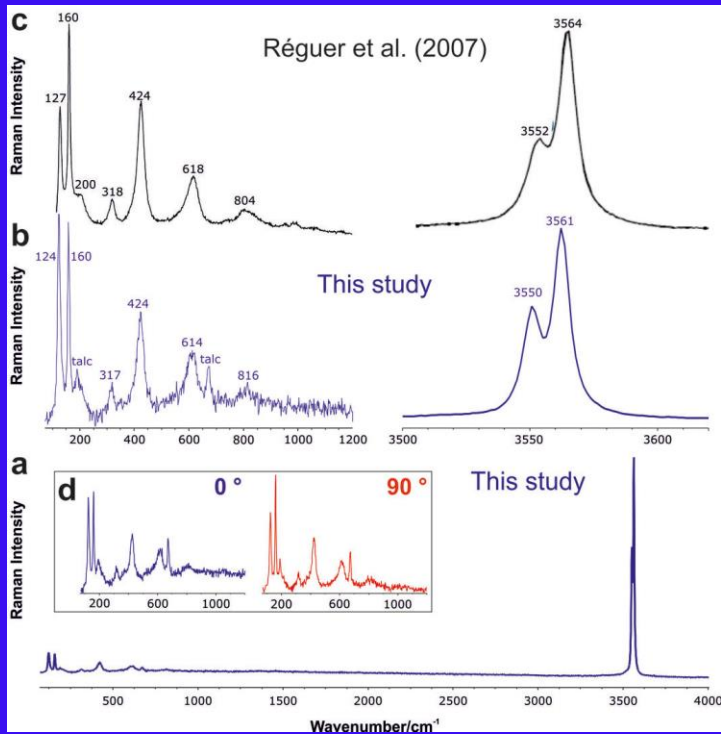


- $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ often found as a product of corrosion of iron interacting with Cl-rich anoxic brines (in archaeology)



Parahibbingite $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ – a new mineral

- Parahibbingite identified by combination of Raman and FIB-SEM-TEM (TEM-EDX and TEM-SAED)



Conclusions – future plans

- BaCl_2 – a new mineral in salt melt inclusions
- publications on genesis of the Rozália mine
- publications on genesis of the Biely vrch deposit
- publication on perlite genesis
- publication on bentonite genesis
- submitted new APVV project: **Complex model of the W-Mo deposit Ochtiná-Rochovce and environmentally acceptable possibilities of its exploitation**