Portable Raman Spectrometers for Geoscience Applications

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Outline

» Raman spectroscopy

» Portable instrumentation

» Examples of geoscience applications

Raman effect - principle

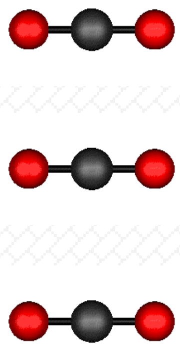
» Inelastic scattering of light

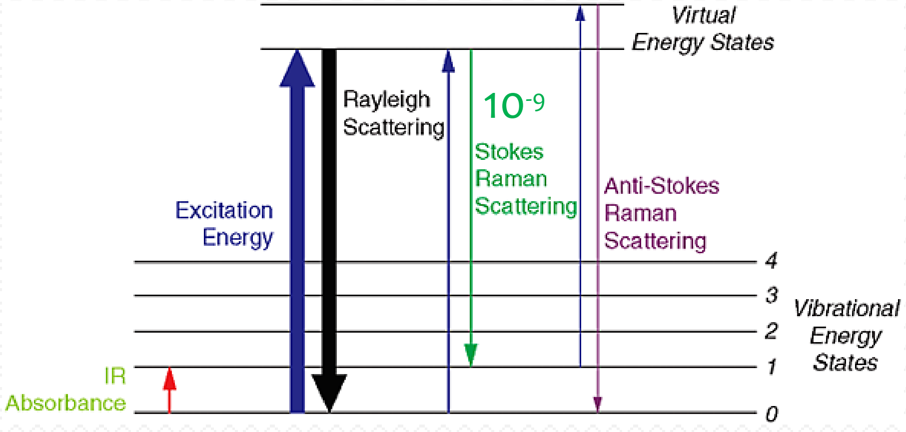
» Discovered in 1928 by C. V. Raman

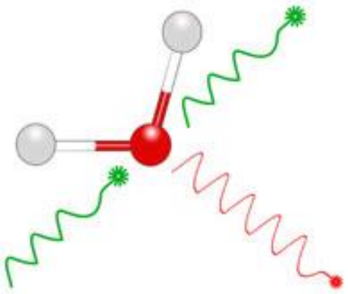
» Molecules excited to a virtual energy state

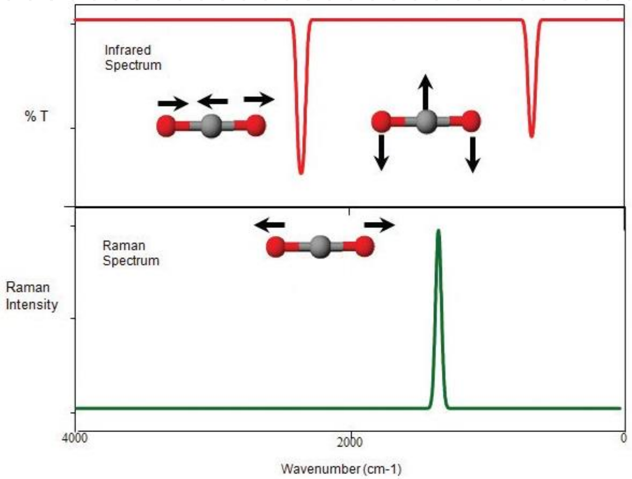
» Emitted light has different wavelengths

» The wavelength differences carry information about chemical bonds and structure of the sample









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Sixth Decennial International Conference on Mineral Exploration
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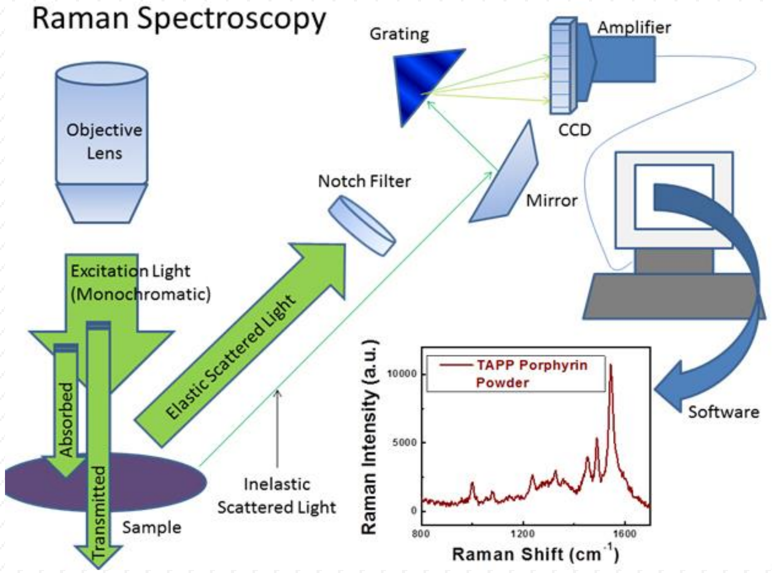
Raman spectroscopy

» Analytical technique based on the Raman effect

» Discovery of lasers in 1960s

» Raman microspectrometers

» Today many advanced techniques (SERS, hyper Raman)



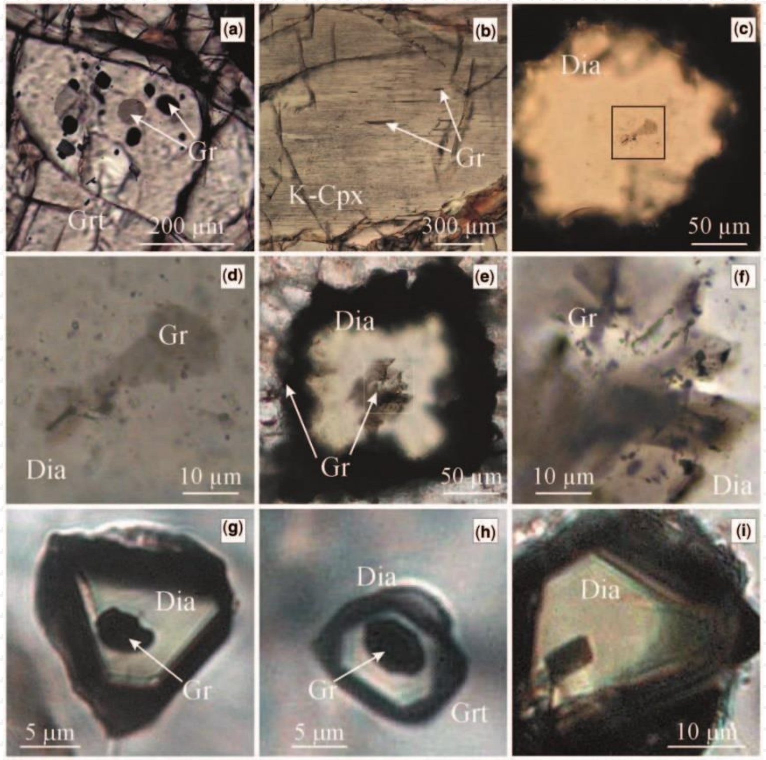
Advantages of Raman spectroscopy

- No pretreatment of samples necessary
- No chemical extraction
- Fast analysis
- Inorganics and organics in one analysis
- Possibility to obtain spectra of micrometric objects
- Possibility to obtain spectra outdoors onsite

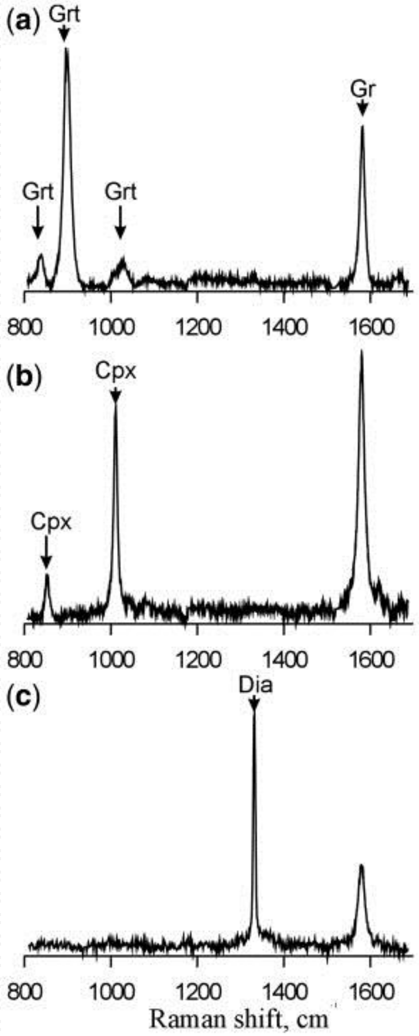
WHY Raman?

Raman spectroscopy in geoscience

Inclusions in UHPM rocks



Korsakov et al., 2010



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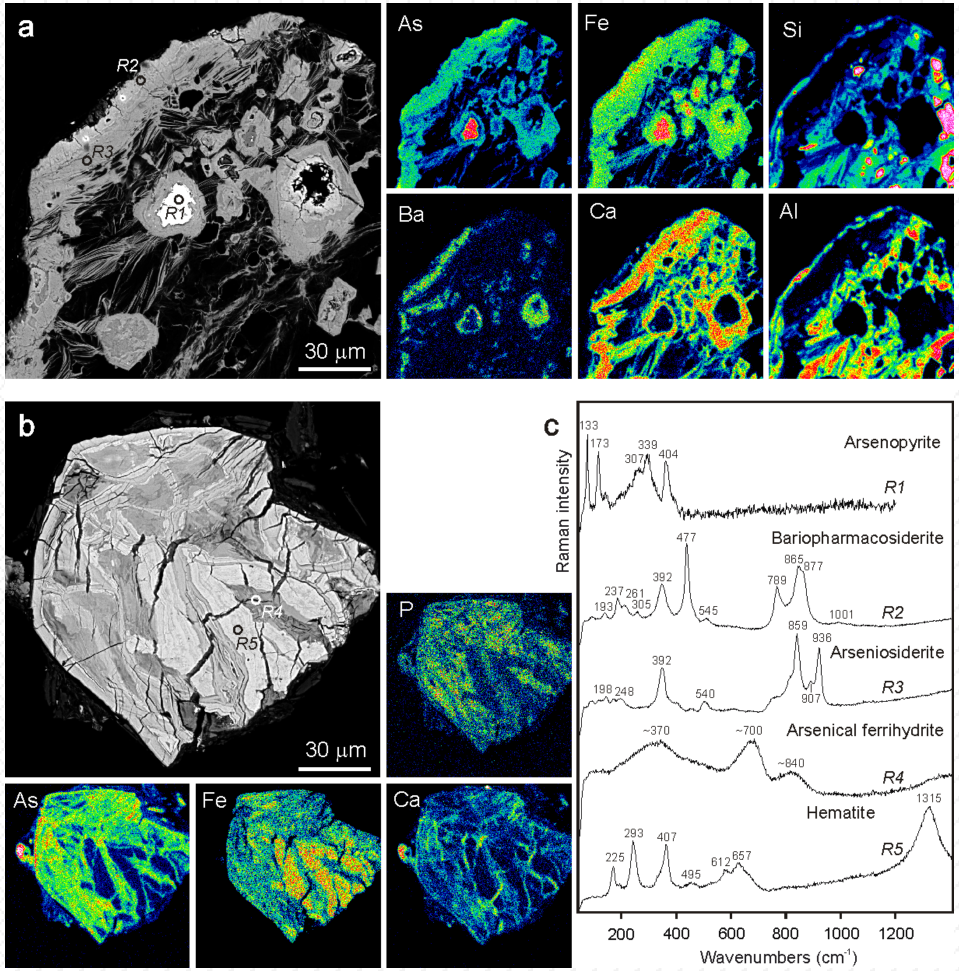
Raman spectroscopy in geoscience

Excellent for mineral phases identification

- Arsenic mineralogy of soils and mining waste at historic Smolotely-Líšnice gold district, Czech Republic
- Micrometric analysis, identification of minerals and more amorphous phases



Drahota et al., 2017

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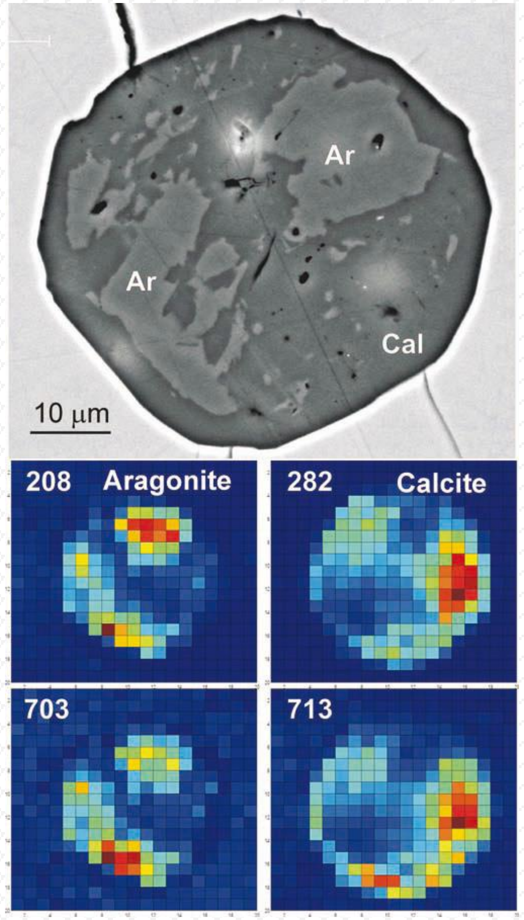
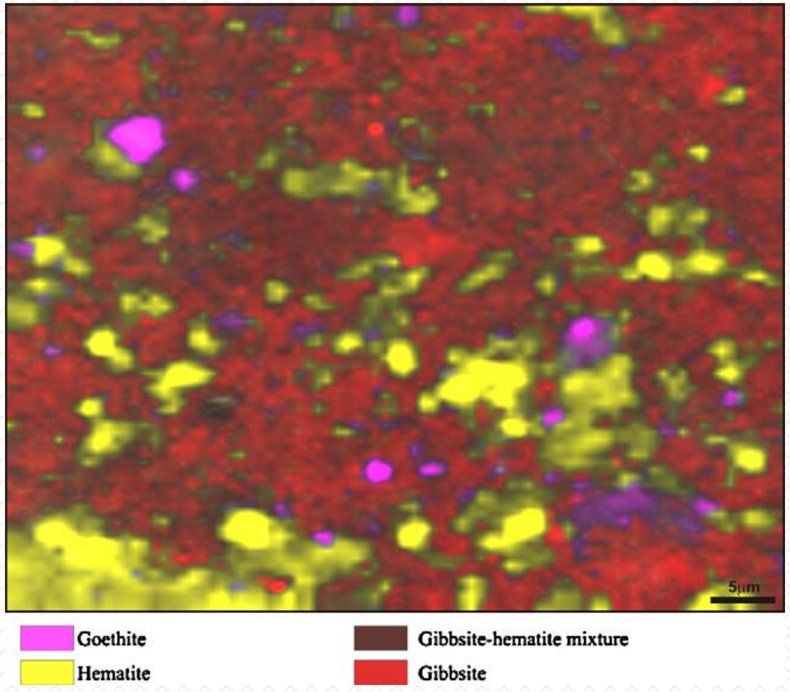
Raman spectroscopy in geoscience

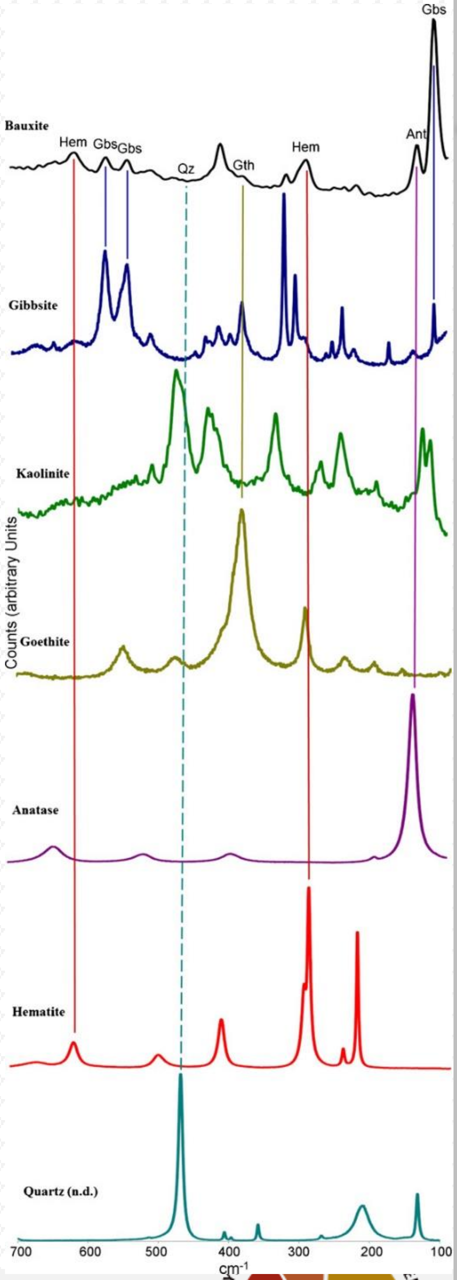
Raman Mapping



Korsakov et al., 2009



Faulstich et al., 2011



Portable versus laboratory spectrometers

Laboratory instruments

» Static, but highly configurable

» Samples have to be brought to a lab

» Highest precision, accuracy and details

» Micrometric measurements, mapping

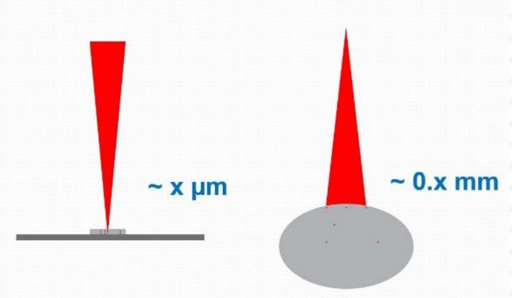
Portable instruments

» Lightweight and flexible

» Fast in-situ analyses

» Generally lower performance

» Larger laser spot sizes



Examples of portable Raman spectrometers

Research using portable instruments

» Mineral identification and in-situ analyses

» Applications in ‘extreme‘ environments (burning coal dumps, underground in mines, Alpine conditions

» Arts and cultural heritage (gemstones, artifacts)

» In-situ studies of pigments of microorganisms

In-situ analyses of minerals at outcrops

- Plešovice quarry, granulites with pegmatic veins
- Anorthite, muscovite, quartz, zircon, apatite, garnet, tourmaline identified using handheld R.s.
- Light vs. dark minerals

In-situ analyses of minerals at outcrops

Mineral	Instrument	in/out	Raman bands					
Quartz	reference		*1082*	*810*	**465**	356	*265*	**207**
	DeltaNu	in			**465**			**214**
	DeltaNu	out			**470**	359		216
	Ahura	out		*804*	**465**	354	265	**210**

Mineral																								
Zircon	Ref 1											1009	975	925	641	547	439	394	357			265	225	202
	Ref 2		Laser-induced fluorescence bands									**1006**	972				**436**		**355**	335			224	
	A	in	*1977*	*1855*	1531		1502	1462	**1379**	1257		1007	*974*		640	*537*	439	386	357		313		228	
	DN	in	*1969*	1853	1534			1466	**1383**	1263		1006		928	*639*	*541*	*437*	391	*359*		318			
	A	out	*1965*	*1840*		1518			**1374**	1259	1225	1003	971		*635*	*544*	436		353		314			

Mineral																			
Muscovite	ref.		1116	1098	1024	958	913	754	**703**	638	**411**	382	316	295	**265**	217	198	172	124
	A	in	1109			955	912	753	**702**	636	**407**	382			**264**	218			
	DN	in						749	**704**	639	**414**				**267**				
	A	out					912		**701**	638	405	384			**265**				

Mineral												
Apatite	ref.		1076	*1047*	**962**		609	589	450	431		
	DN	in	1075		**964**	730		588			309	267
	A	out	1067	*1050*	**964**			*588*		*431*		

Legend: **strong band**, normal band, *weak band*, reference1, reference2

Sulfates - Valachov

- Locality in Czech republic, pyrite-bearing shists
- cca. 1850s mining mostly for pyrite for production of sulfuric acid
- ubiquitous presence of secondary crusts consisting mostly of Fe and Ca sulfates and iron oxohydroxides

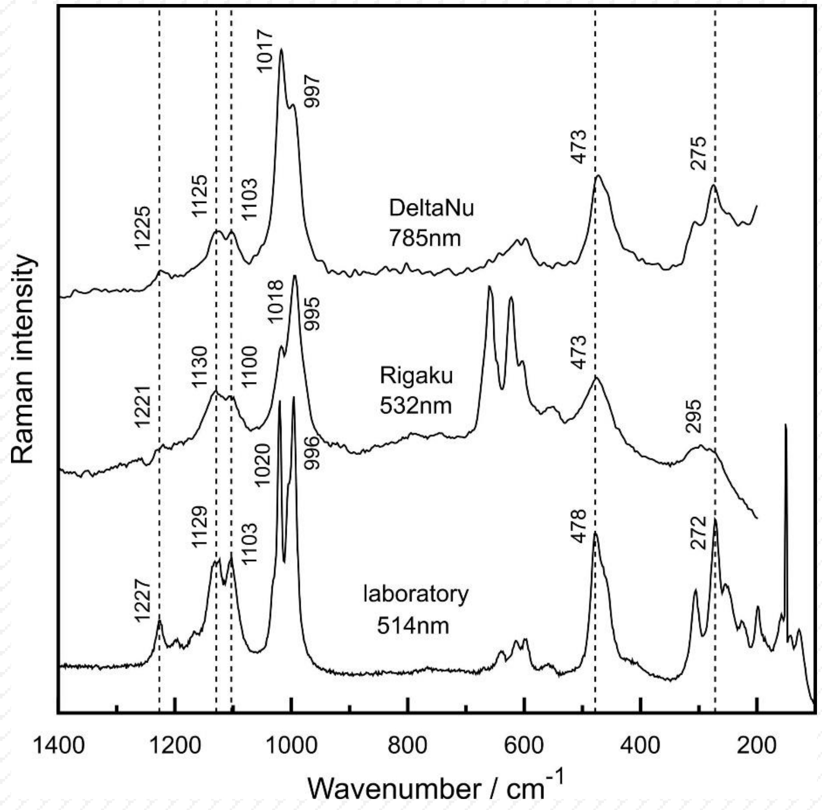
Sulfates - Valachov

- In-situ analyses using 532 and 785 nm handheld instruments
- Identification of sulfates in natural relatively complex associations

Sulfates - Valachov

» Based on the interpretation of the Raman spectra, gypsum, rozenite, melanterite, fibroferrite, magnesiocopiapite, and jarosite were identified within the collected samples.

Raman spectra of magnesiocopiapite
$(Mg,Fe^{2+})Fe^{3+}(SO_4)_6(OH)_2 \cdot 20(H_2O)$



Burning coal dumps

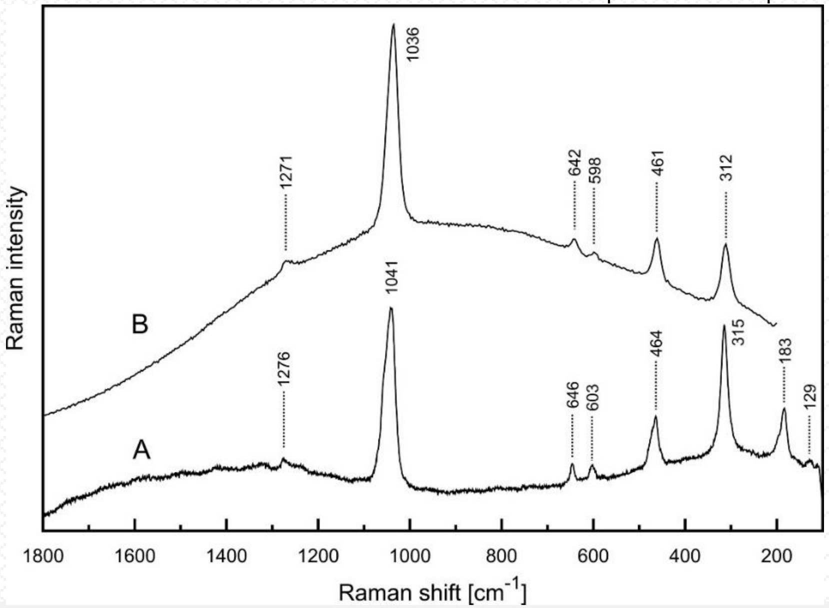
Burning coal dump - Heřmanice

- Clastic Upper Carboniferous sediments, bituminous coal seams
- Dump material accumulated from 1850s till 1993
- Underground combustion for decades, currently remediated
- Fumarolic-like mineral associations together with secondary sulf.

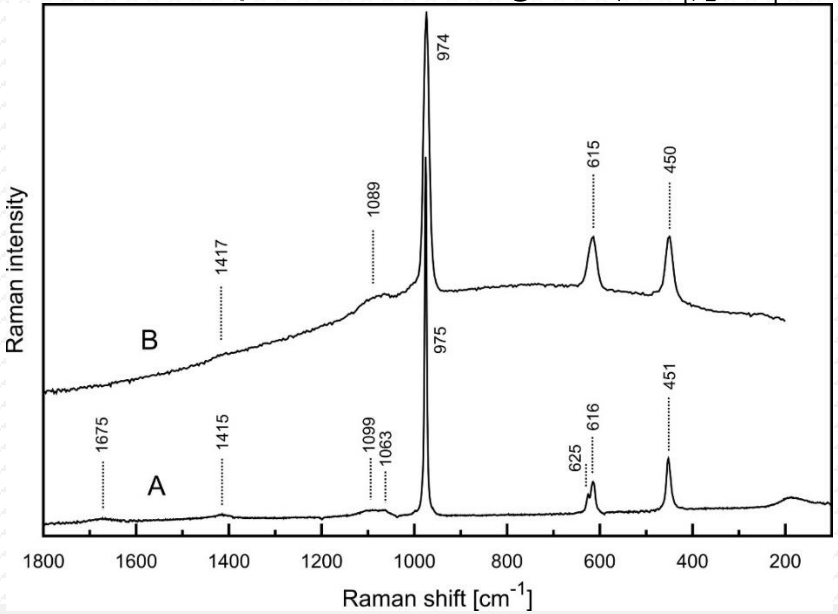
Burning coal dump - Heřmanice

- Identified minerals: native sulfur, sal ammoniac, mascagnite, letovicite, sabieite, godovikovite, efremovite, and pyracmonite

Raman spectra of sabieite $(NH_4)Fe^{3+}(SO_4)_2$



Raman spectra of mascagnite $(NH_4)_2SO_4$



Burning coal dump - Anna

» Lower temperature environment

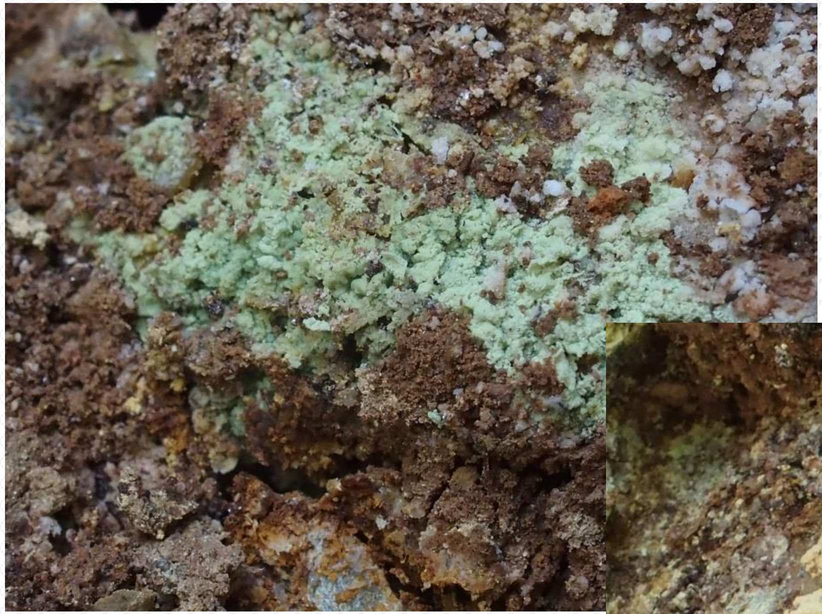
» Similar sulfate-rich mineralogy

» Work in progress

Arsenates – Kaňk, Kutná Hora

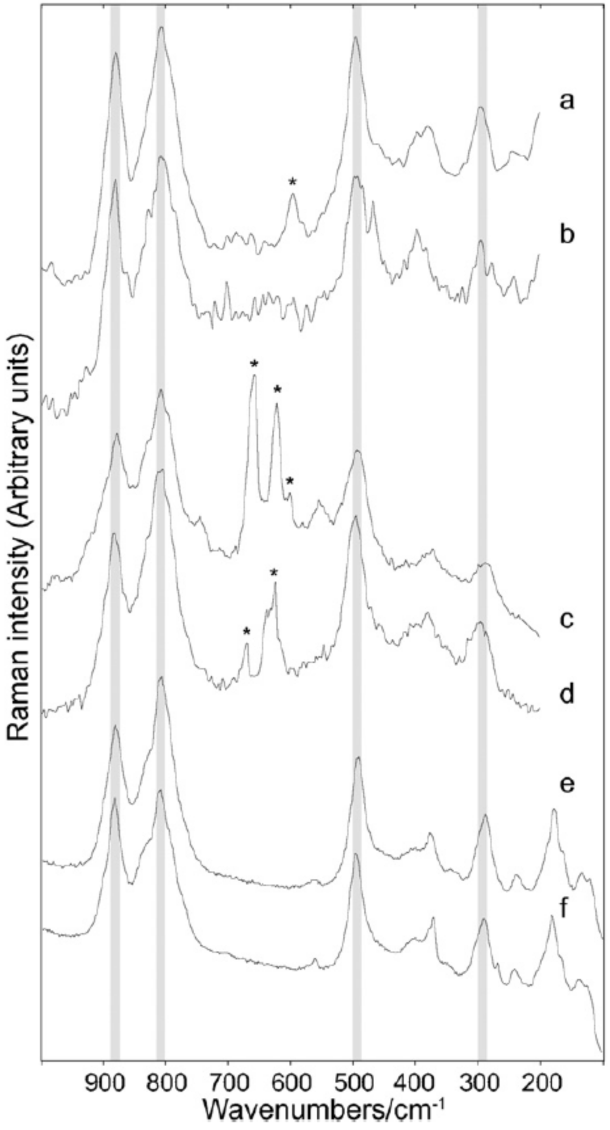
- Locality in Czech republic, highly weathered mine dumps after historic silver, arsenic and copper mining
- Primary arsenopyrite in association with secondary arsenates and other minerals
- As contaminated soil and ground water

Arsenates - Kaňk



Arsenates - Kaňk

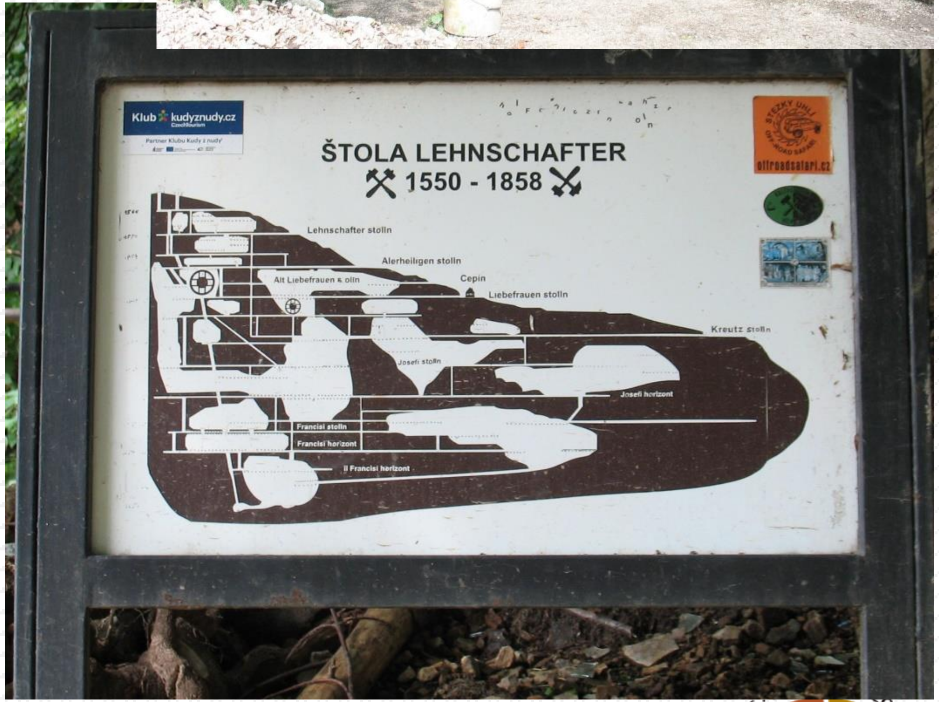
» Bukovskýite, kaňkite, parascorodite, and scorodite were identified in situ using portable Raman instruments



Raman spectra of kaňkite
$Fe^{3+}AsO_4 \cdot 3.5(H_2O)$

Arsenates - Lehnschafter

- Locality in Ore Mountains, Czech republic, historic silver mine complex
- Slowly being re-opened for visitors
- Secondary arsenate minerals, deposited on walls and galleries
- Considerable secondary As mineralization, esp. zýkaite

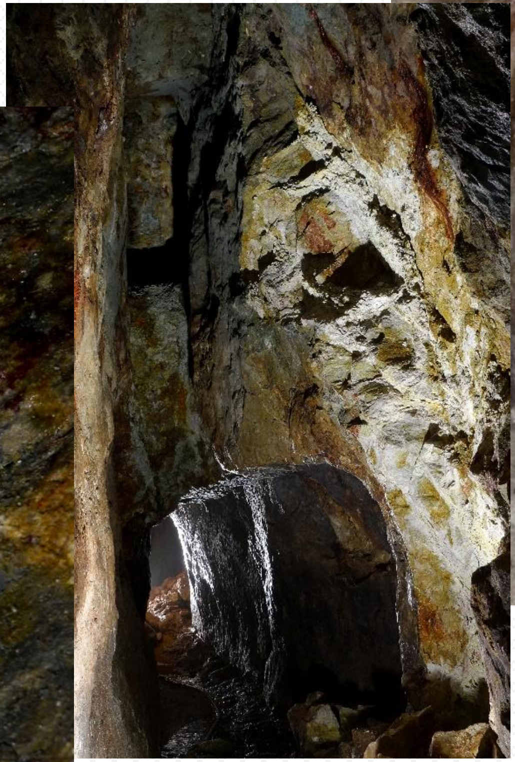


Arsenates - Lehnschafter

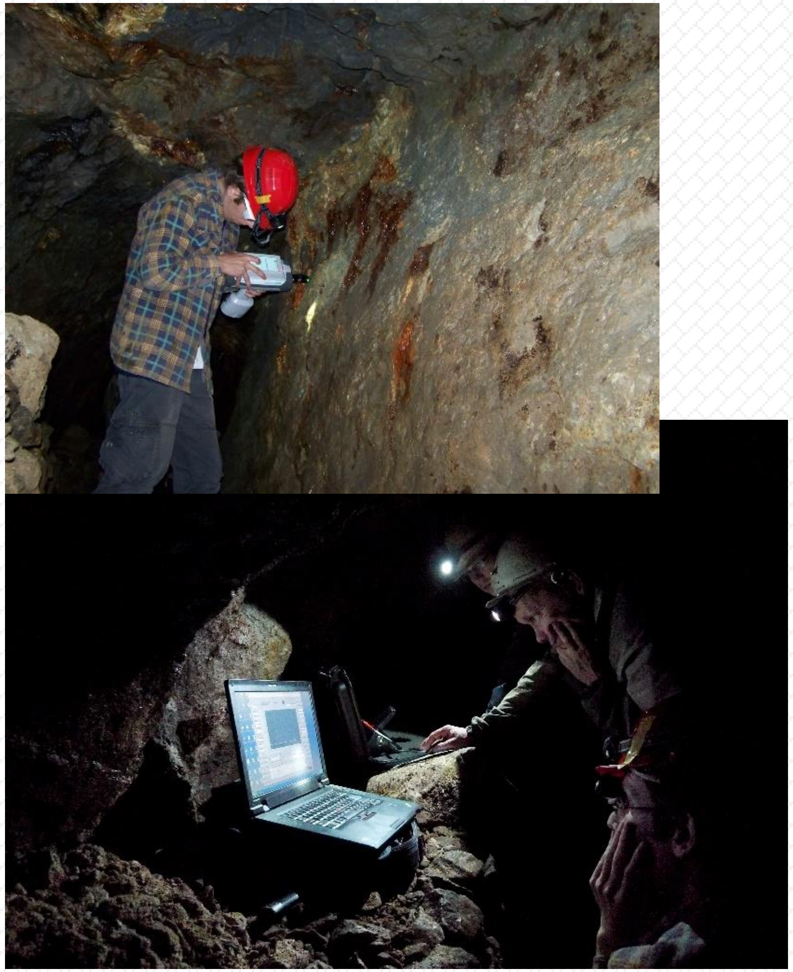
» Challenging in-situ measurements

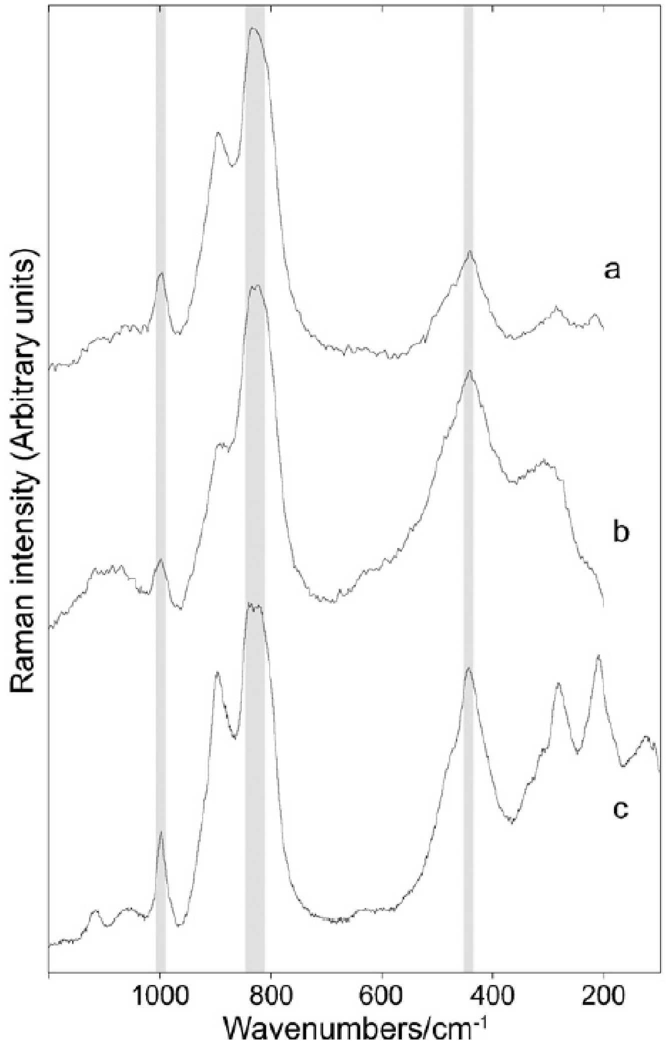
» Deep in the mountain (200 m tunnel)

» Very high humidity, condensing water may damage instruments



Arsenates - Lehnschafter





Raman spectra of zýkaite

Applications in cultural heritage and arts

- Identification of gemstones, exposing fakes or subtitutes
- In-situ identification of pigments (anorg. and org.)
- Precious artifacts, cannot be sampled, or even moved to a lab > portable instrumentation
- Fast analyses

Ring monstrance

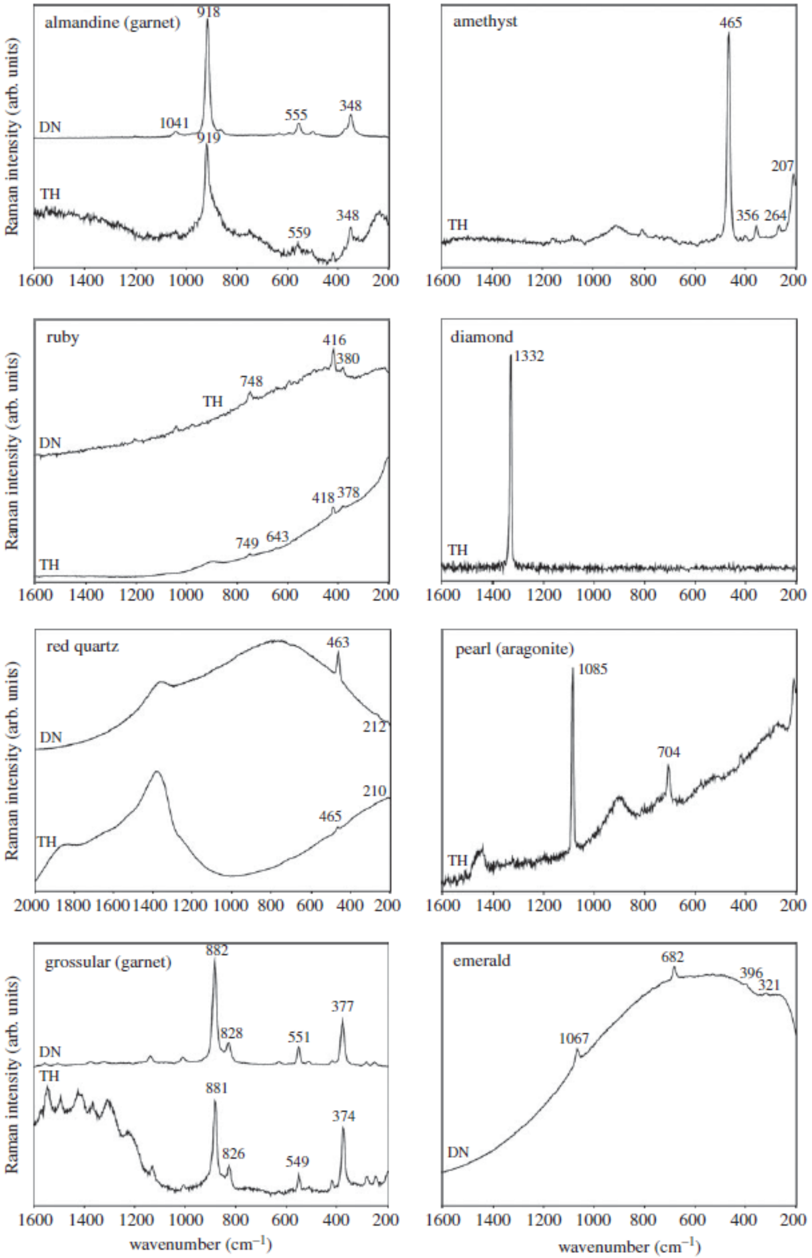
- Religious artifact (1748) made fo Loreto, Prague
- Huge historical value
- Heavily decorated with 65 mounted jewels and 324 stones
- Great number of 'diamonds'

Ring monstrance

» Over 200 Raman spectra collected in a few hours using handheld and palm instruments

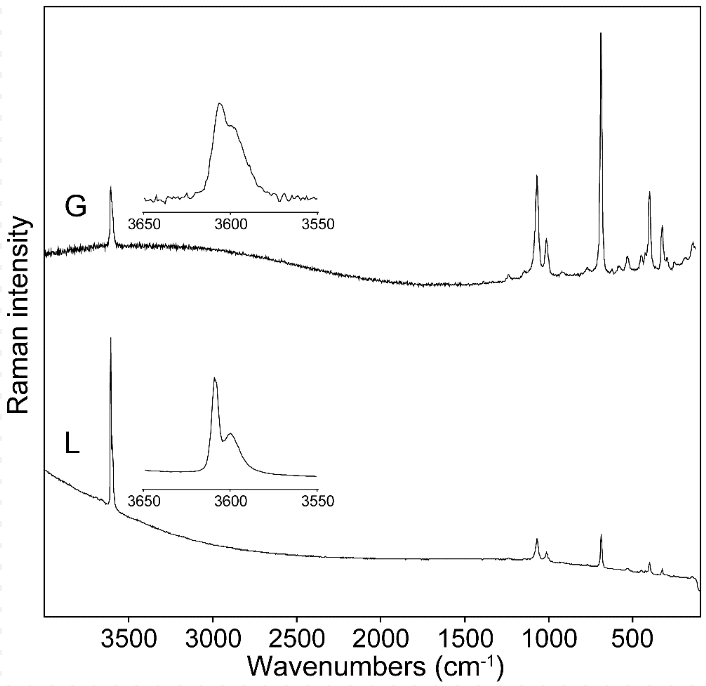
» All diamods were confirmed plus other stones such as emerald, rubies, sapphire, amethysts, garnets

Ring monstrance



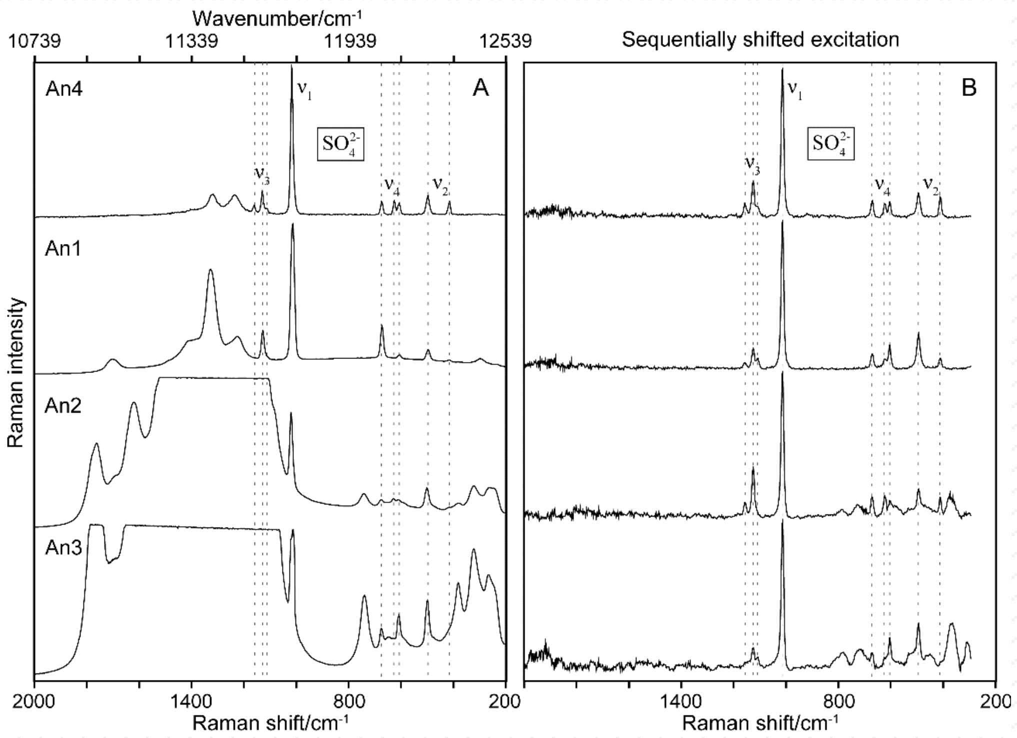
Recent advances in portable instruments

- Overall improvement of performance and data output getting closer to the laboratory spectrometers
- Spectral region up to 4000 cm^{-1} accessible: OH stretching vibrations, genetic studies of emeralds



Recent advances in portable instruments

- Sequentially shifted excitation
- Suppression or elimination of fluorescence from the Raman spectra
- Very useful for natural samples of minerals (REE, and other elements form fluorescence centers)



Conclusions

- Portable Raman spectrometers are powerful tools for geoscience research
- Applications include *in-situ* mineral identification at outcrops – a possible tool for mineral exploration, fast and non-destructive identification of gemstones, inorganic and organic pigments detection
- Instruments are rapidly improving technologically -> greater scientific output, i.e. fluorescence suppression

Acknowledgements

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Merci pour votre attention!