RAMAN SPECTROSCOPY AND IMAGING: USEFUL TOOLS IN THE STUDY OF MINERALS AND FLUIDS IN HP/UHP METAMORPHIC ROCKS

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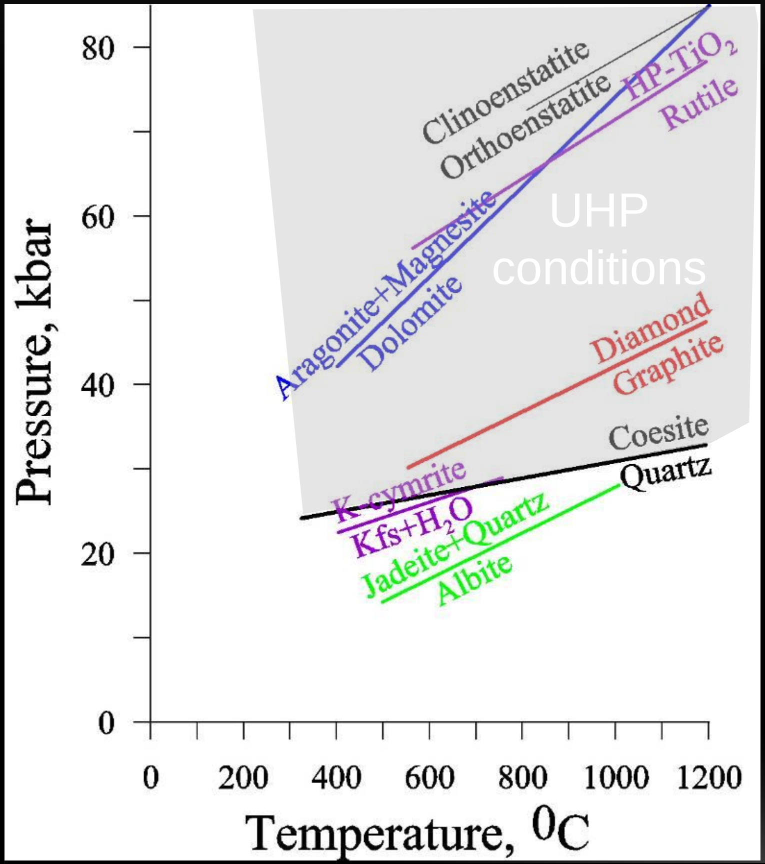
School of Mining & Metallurgical Engineering

National Technical University of Athens, Greece

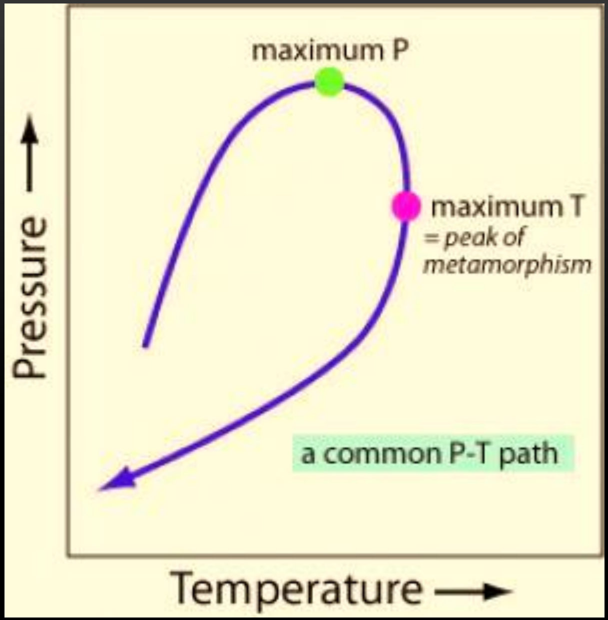
High Pressure (UHP) metamorphic conditions



Pressure and temperature stability of various mineral phases that are of relevance to UHP metamorphism (after Massonne, 2005).

- **Ultra high pressure** (**UHP**) metamorphic rocks of common basic to felsic nature are defined by the occurrence of coesite, a silica polymorph that is denser than quartz. According to several experimental studies, the transition from quartz to coesite at 600°C requires a pressure (P) of around 27 kbar, a temperature (T) of conditions that occur on Earth at depths close to 100 km.

Metamorphic Petrology / (U)HP Metamorphic Rocks



- What is important in Metamorphic Petrology?
  - To determine the **Peak** Metamorphic Conditions
  - To reveal the subduction and exhumation path

- What is the methodology?
  - Conventional geothermometers and geobarometers
  - Thermodynamics softwares based on internally consistent thermodynamic datasets (THERMOCALC, TWQ, PERPLEX, etc)

Raman Spectroscopy in (U)HP Metamorphic Rocks

Inclusions

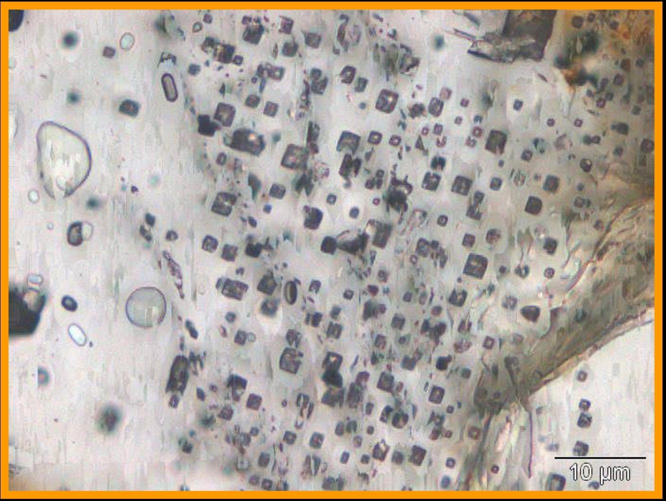
- (U)HP Polymorphs
  - C Graphite / Diamond
  - SiO_2 Quartz / Coesite
  - $CaCO_3$ Calcite / Aragonite
  - Al_2SiO_5 Sillimanite (/Andalousite) / Kyanite
  - TiO_2 Anatase / Rutile / TiO_2 with α-PbO structure
  - $NaAlSi_3O_8$ Albite / Kumdykolite
  - $KAlSi_3O_8$ Orthoclase (Microcline-Sanidine) / Kokchetavite
  - … … … … …
- Multiphase Fluid/Melt inclusions
- Internal stress / overpressure

Exsolutions

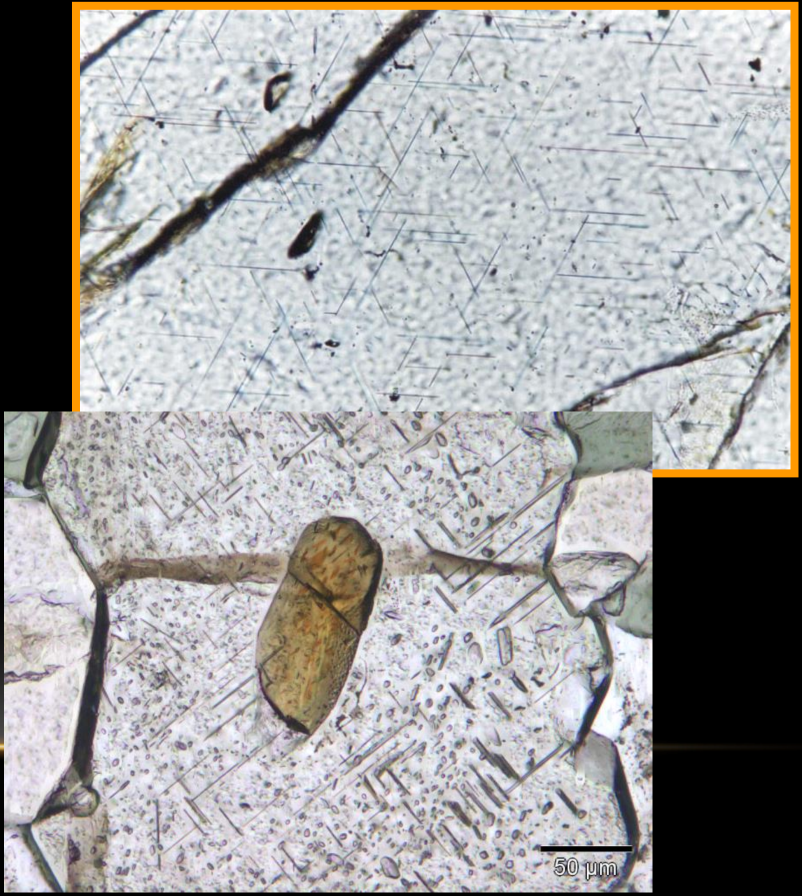
Raman Spectroscopy in (U)HP Metamorphic Rocks

- ☐ Not well-identified optical properties because of small size
- ☐ Beneath the thin section surface → SEM study impossible

Inclusions



Exsolutions



Raman Spectroscopy in (U)HP Metamorphic Rocks

Inclusions

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  - C Graphite / Diamond
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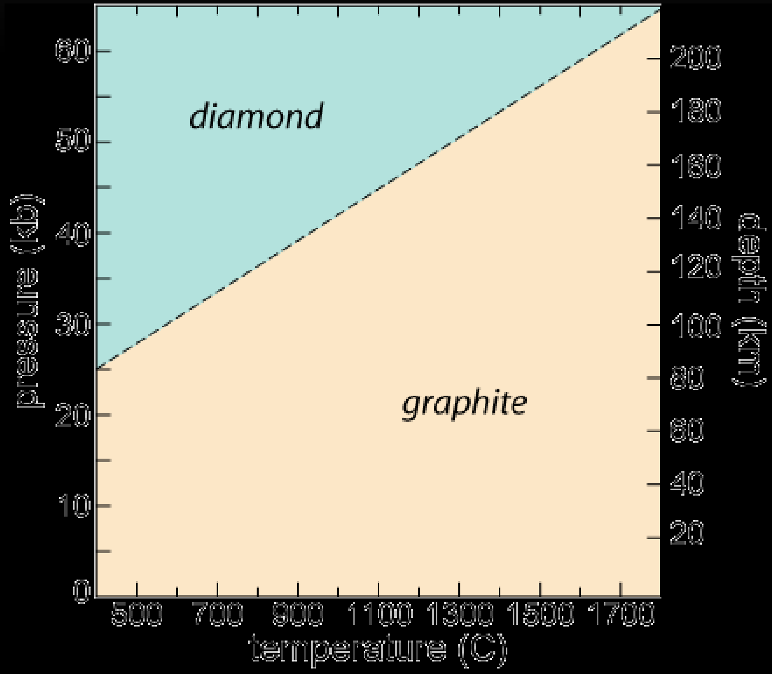
  - TiO2 Anatase / Rutile / TiO2 with α-PbO structure
  - NaAlSi3O8 Albite / Kumdykolite
  - KAlSi3O8 Orthoclase (Microcline-Sanidine) / Kokchetavite
  - … … … … …
- Internal stress / overpressure

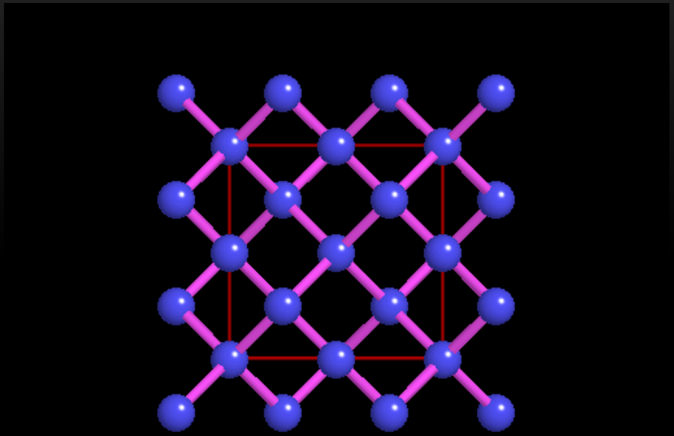
Exsolutions

C-polymorphs (Graphite-Diamond-Lonsdaleite)

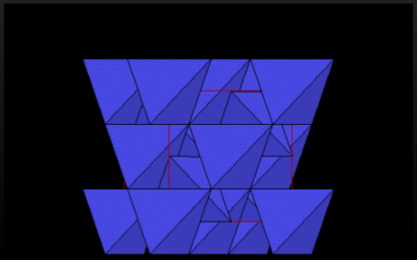
- Raman spectroscopy
  - very sensitive to the nature of carbon bonding → Important non-destructive characterization tool for distinguishing micro-sized particles of C polymorphs,
  - Very useful in the study of C micro- inclusions not exposed at the polishing surface, since it gives the opportunity of focusing onto different depths into the sample (e.g. Nasdala & Massonne, 2000).

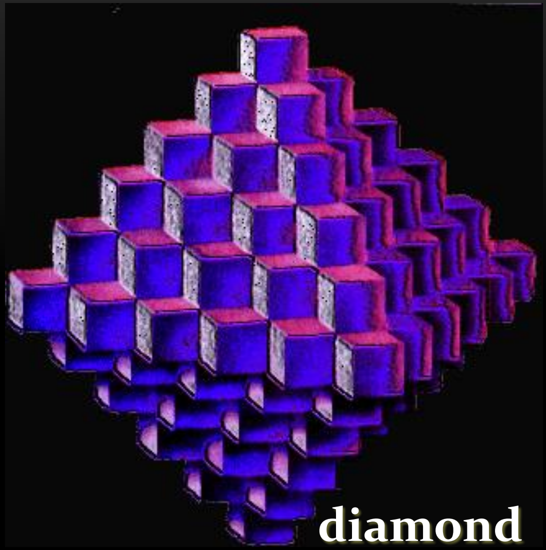


Diamond

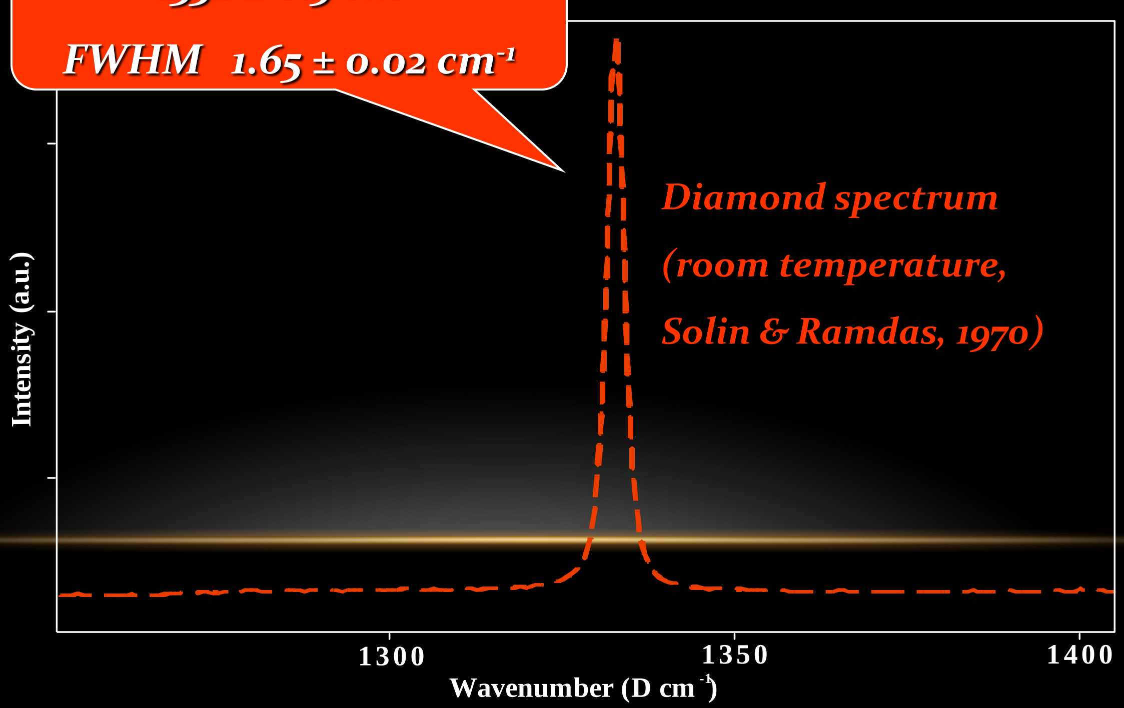


diamond





diamond



1332 ± 0.5 cm^{-1}

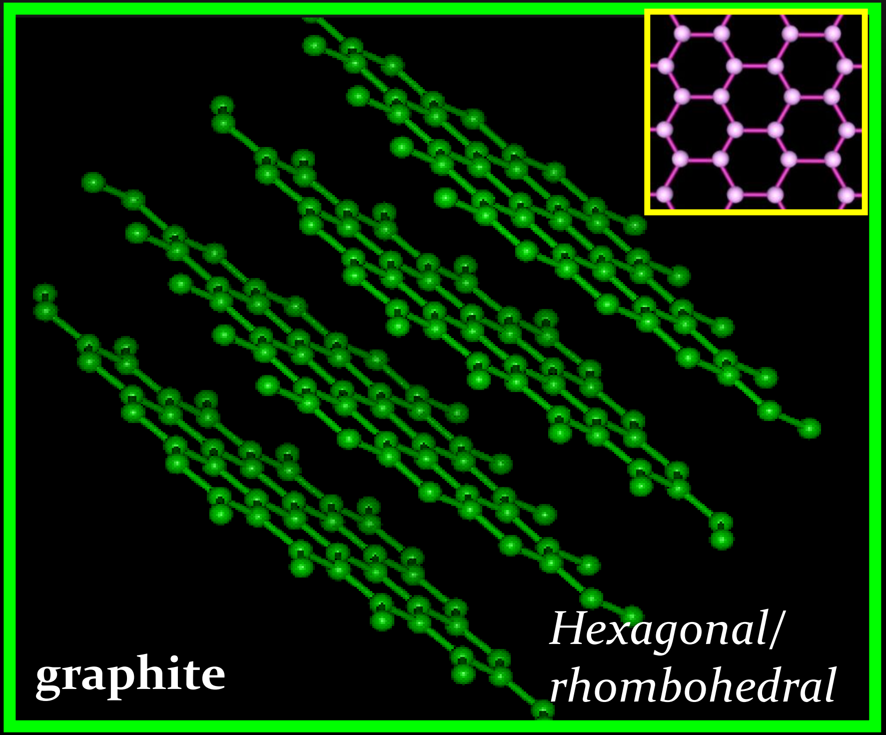
FWHM 1.65 ± 0.02 cm^{-1}

Diamond spectrum

(room temperature,

Solin & Ramdas, 1970)

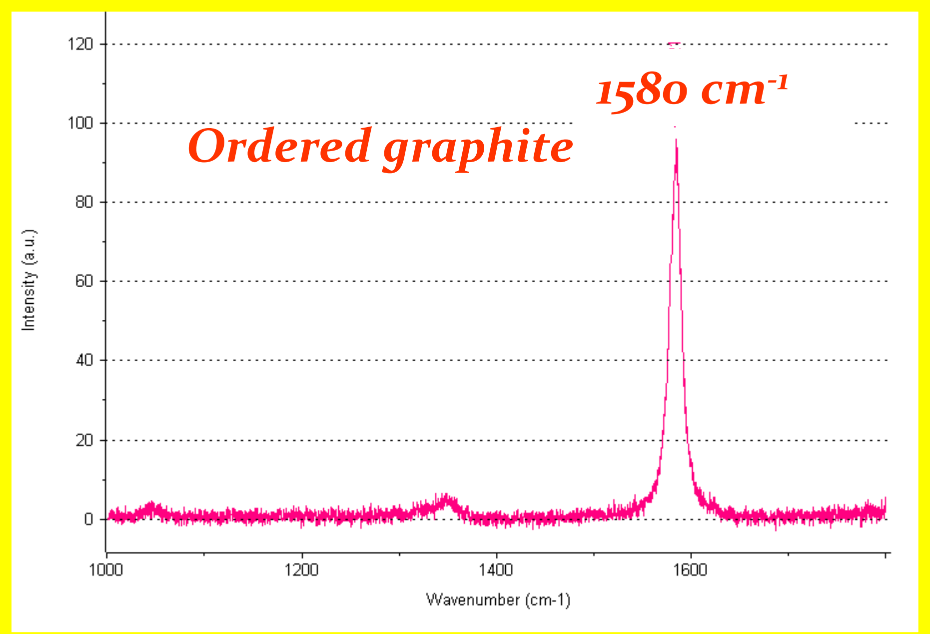
Graphite

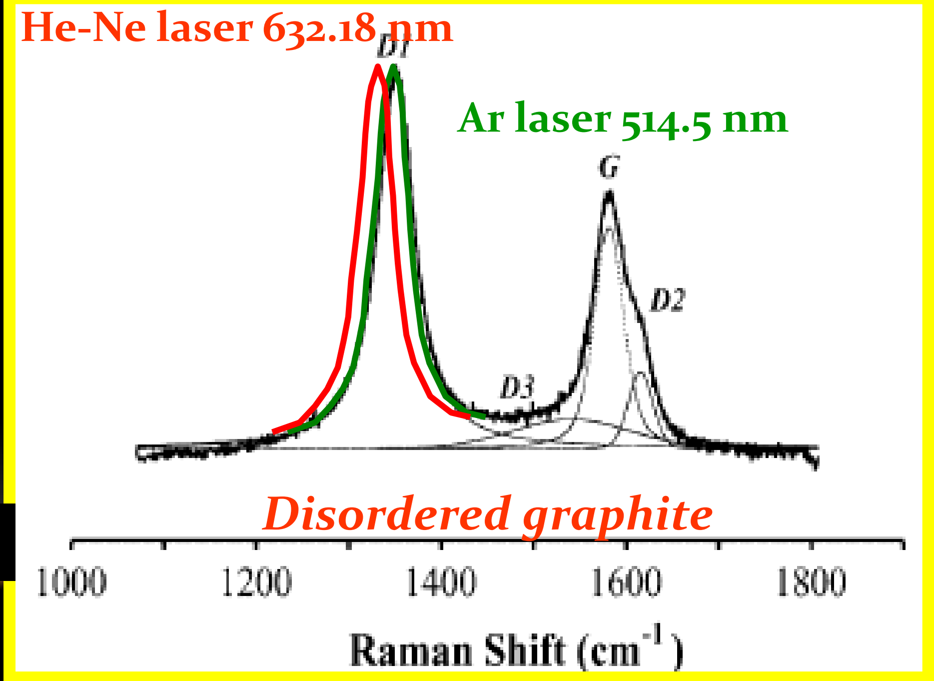


Graphite

Ordered graphite: 1580 cm^{-1}

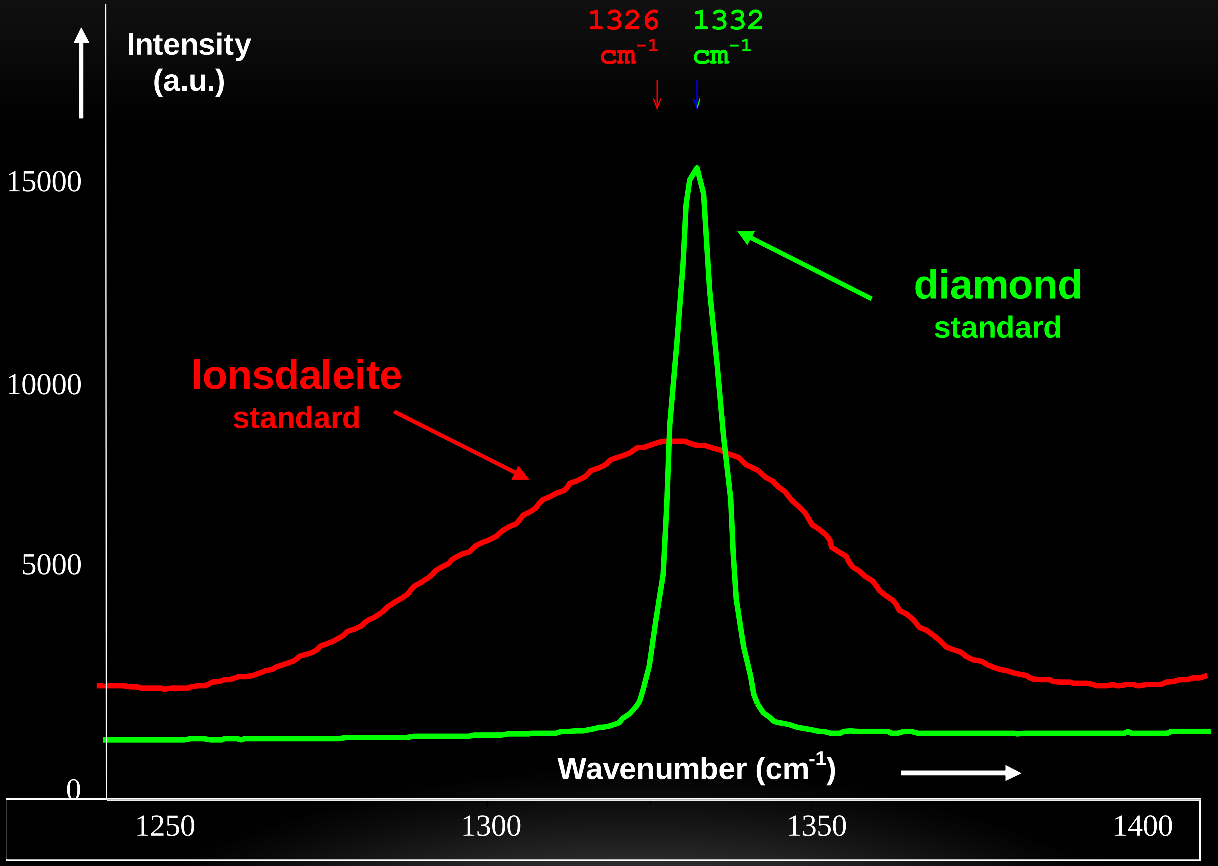
**Disordered graphite: D1 1330-1340 cm^{-1}
D2 1620 cm^{-1}, D3 1500 cm^{-1}**





decreasing laser energy → Shift of the D band to lower wavenumbers (Matthews et al., 1999)

Lonsdaleite (hexagonal diamond)



Raman spectrum of a lonsdaleite standard (from SMITH, D C (2008) revealing that it is centred slightly to the left of diamond and is much wider and weaker.

First metamorphic Diamond reported

LETTERS TO NATURE

Diamond inclusions in garnets from metamorphic rocks: a new environment for diamond formation

N. V. Sobolev & V. S. Shatsky

Institute of Geology and Geophysics, Siberian Division of the USSR Academy of Sciences, 630090 Novosibirsk 90, USSR

Diamonds commonly occur in kimberlites, lamproites and alluvial sediments derived from these rocks. More recently, diamonds (or their graphite pseudomorphs) have been discovered in ultramafic massifs[1] and picrites[2]. Here we report the occurrence of diamonds in situ in crustal rocks: highly retrograded high-pressure metamorphic garnet–pyroxene and pyroxene–carbonate–garnet rocks, biotite gneisses and schists from the Kokchetav massif, northern Kazakhstan, USSR. The diamonds are cubo-octahedral, averaging 12 μm in size, and occur in zircons, and with euhedral graphite as inclusions in unzoned garnets. We believe that the zircon and garnet matrices protected these diamonds from retrogressive transformation to graphite. Mica, rutile, titanite, clinopyroxene, kyanite and zircon also occur as inclusions in garnet, often intergrown with the diamonds. Equilibration relations of inclusions and host garnets indicate that both diamonds and graphite crystallized from a fluid phase under static conditions at pressures of ≥40 kbar and temperatures >900–1,000 °C.

The Kokchetav Massif is a large (~60,000 km²) fault-bounded body of Proterozoic metamorphic rocks surrounded by Caledonian rocks of the Ural-Mongolian fold belt. It is a part of the Central Asian Belt, the major collision zone of Asia[3]. Geological relationships indicate that the massif was emplaced near the end of the Precambrian[4]. The massif core, where diamondiferous rocks occur, consists of a variety of crystalline schists and gneisses, eclogites, pyroxenic granulites, amphibolites, quartzites, marbles and associated calc-magnesite-silicate rocks of amphibolite and granulite facies. Granitic rocks constitute over ~65% of the present exposure. The mineralogy of the eclogites has recently been reviewed[5], and suggests equilibration conditions of 900 °C, ≈18 kbar, for the eclogites associated with the diamond-bearing rocks, and 600–700 °C, 12–14 kbar, for eclogites in the eastern portion of the massif.

A garnet–clinopyroxene Sm–Nd age of 533 ± 20 Myr dates the end of high-pressure metamorphism. The diamondiferous rocks seem to have differentiated >2 Gyr ago based on interpretation of a whole-rock Pb–Pb isochron[6].

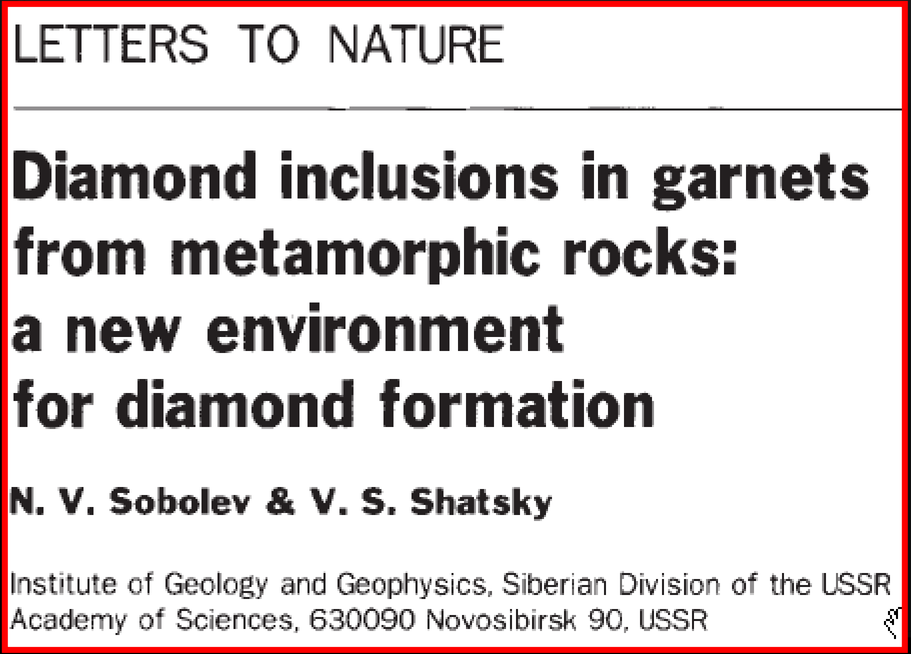
The diamonds occur mainly as inclusions in garnets in garnet–pyroxene, pyroxene–carbonate–garnet rocks, garnet–biotite gneisses and schists. These rocks occur as small lenticular, banded or vein-like bodies within plagioclase gneisses of the Zerendinsk rock series.

Garnet–pyroxene rocks are coarse-grained with euhedral to subhedral garnet (20–40 modal %) and clinopyroxene (50–80%), with interstitial calcite. Accessory minerals include rutile and titanite, secondary chlorite, quartz and K-feldspar. The pyroxene–carbonate–garnet rocks are characterized by large porphyroblasts of clinopyroxene, which are set in a slightly cataclastic matrix of mica and calcite. Garnet grains (up to 1 mm in size, 1–3 modal %) occur randomly throughout the rock.

Schists and gneisses are medium-grained rocks with widely varying modes of plagioclase, quartz, garnet, K-feldspar, biotite and chlorite. Graphite, zircon, apatite and sulphides are accessory. The diamonds are distributed heterogeneously within a given rock and seem to be concentrated in zones or layers, which are otherwise undistinguished in mineralogy. Garnet is relict and is usually replaced by biotite, K-feldspar and chlorite; plagioclase is locally saussuritized. In some samples several grains of clinopyroxene are present, which are partly altered to amphibole and chlorite. Kyanite is also sometimes observed.

Identification of diamond inclusions was made by optical microscopy and Raman spectroscopy on 0.3-mm-thick doubly polished plates of garnet-bearing rocks, as well as by X-ray diffraction and scanning electron microscopy of inclusions extracted from the host garnet. Mineral analyses were obtained

FIG. 1 Diamond inclusions in garnets from metamorphic rocks. *a*, Abundant diamonds intergrown with mica flakes. *b*, A single mica flake with two diamonds and a graphite crystal (dark). *c* and *d*, Diamond intergrowths with rutile. Scale bar is 40 μm for all photographs.



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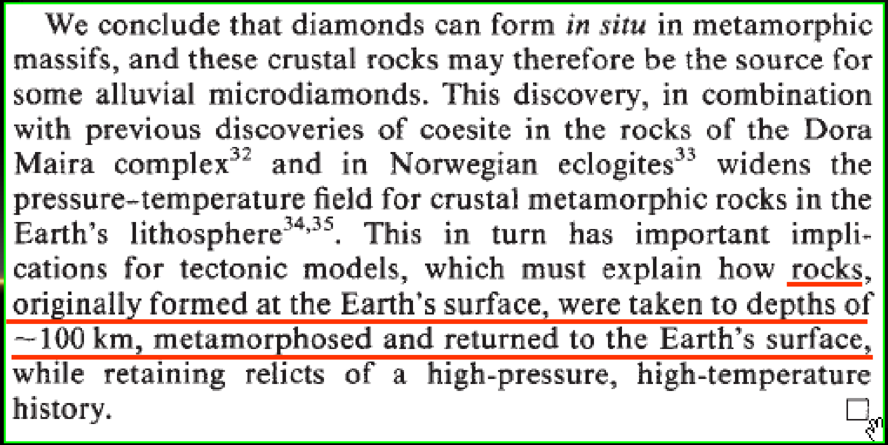
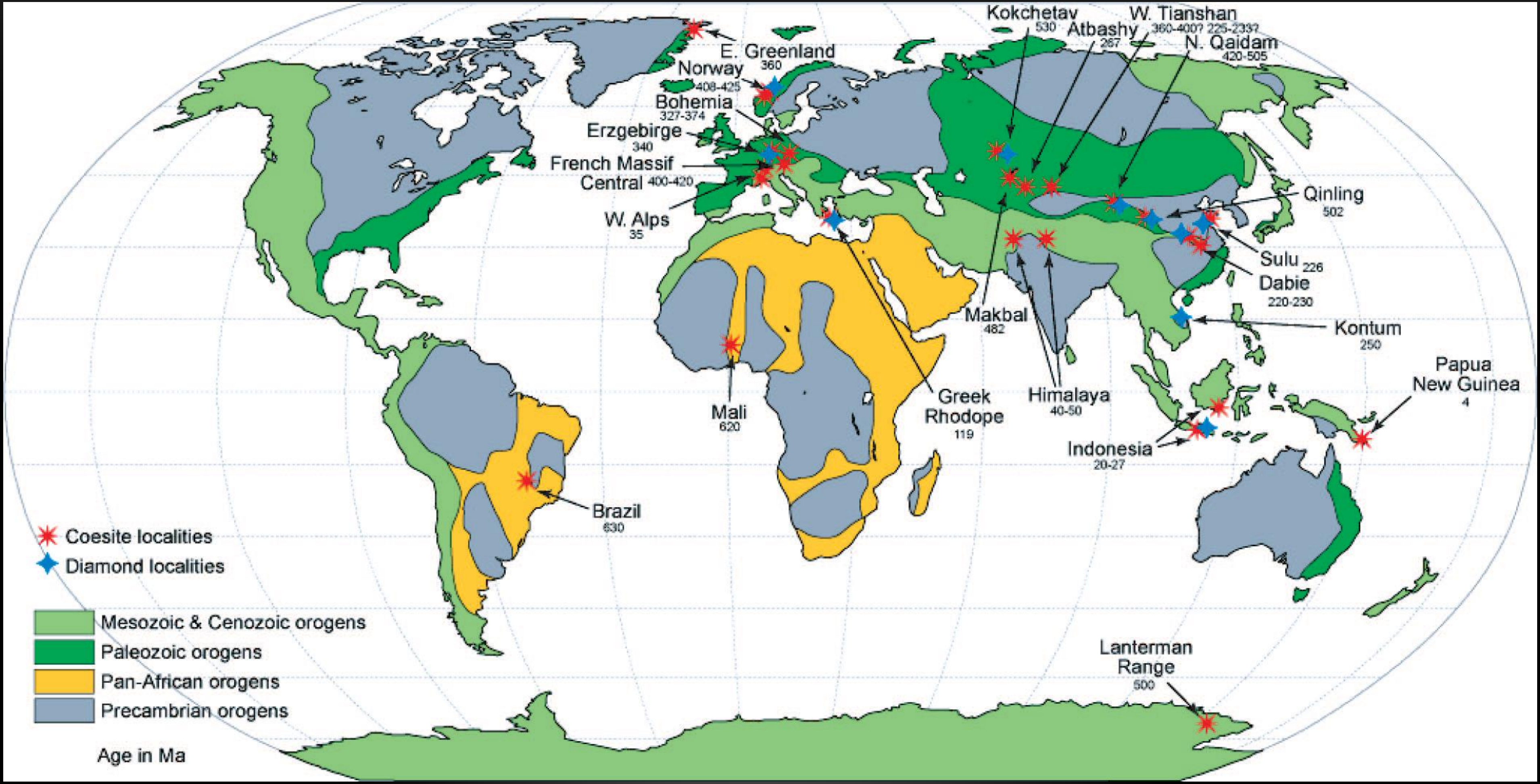


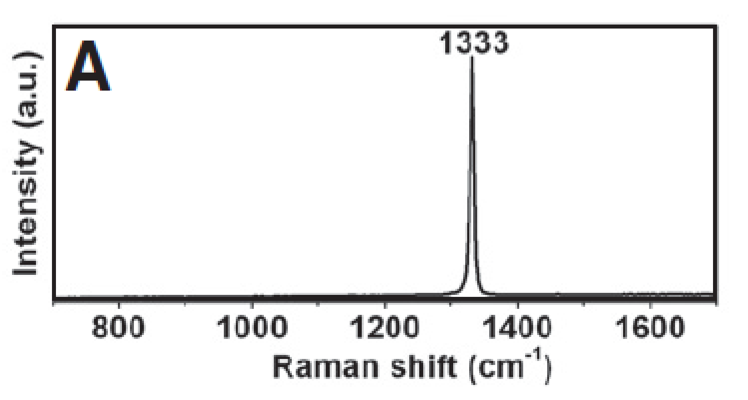
We conclude that diamonds can form *in situ* in metamorphic massifs, and these crustal rocks may therefore be the source for some alluvial microdiamonds. This discovery, in combination with previous discoveries of coesite in the rocks of the Dora Maira complex[32] and in Norwegian eclogites[33] widens the pressure–temperature field for crustal metamorphic rocks in the Earth's lithosphere[34,35]. This in turn has important implications for tectonic models, which must explain how rocks, originally formed at the Earth's surface, were taken to depths of ~100 km, metamorphosed and returned to the Earth's surface, while retaining relicts of a high-pressure, high-temperature history. □



From Liou, 2007

Diamond and coesite discovered in Saxony-type granulite: Solution to the Variscan garnet peridotite enigma

Jana Kotková[1,2,3]*, Patrick J. O'Brien[1], and Martin A. Ziemann[1]
[1]Institut für Erd- und Umweltwissenschaften, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, 14476 Potsdam-Golm, Germany
[2]Czech Geological Survey, Klárov 3, 118 21 Praha1, Czech Republic
[3]Institute of Geosciences, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic



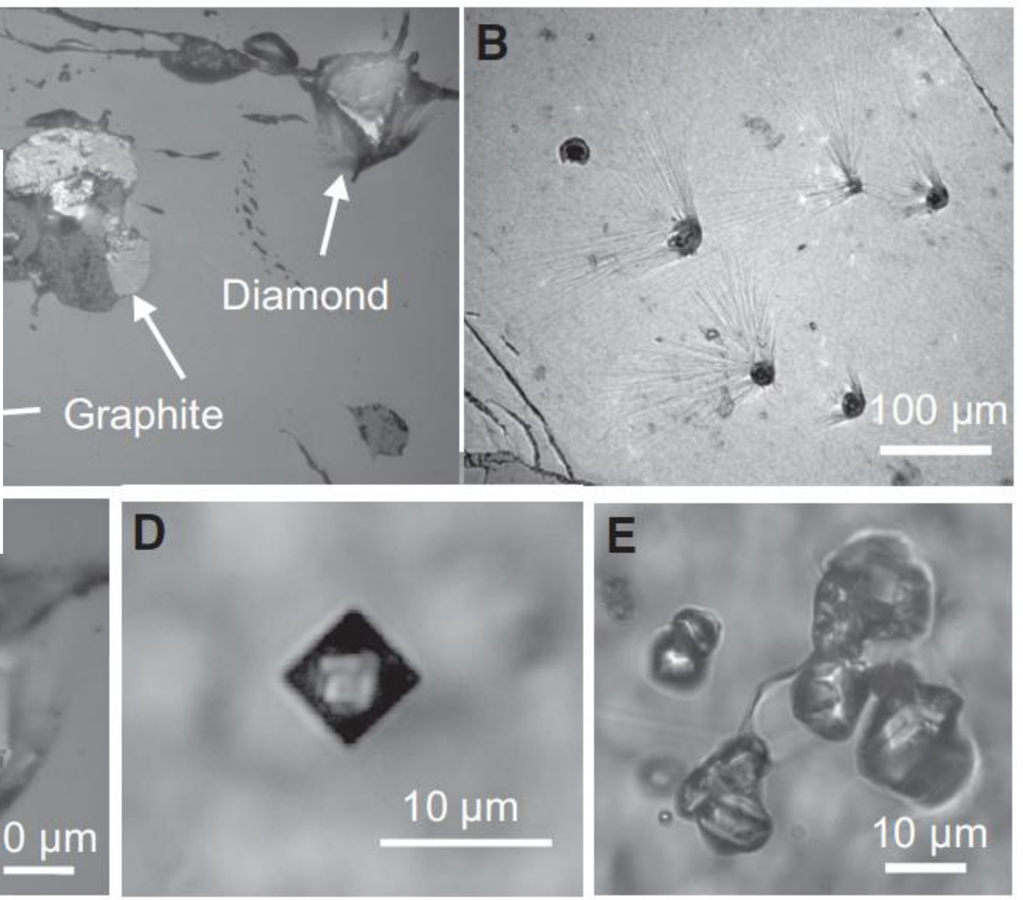
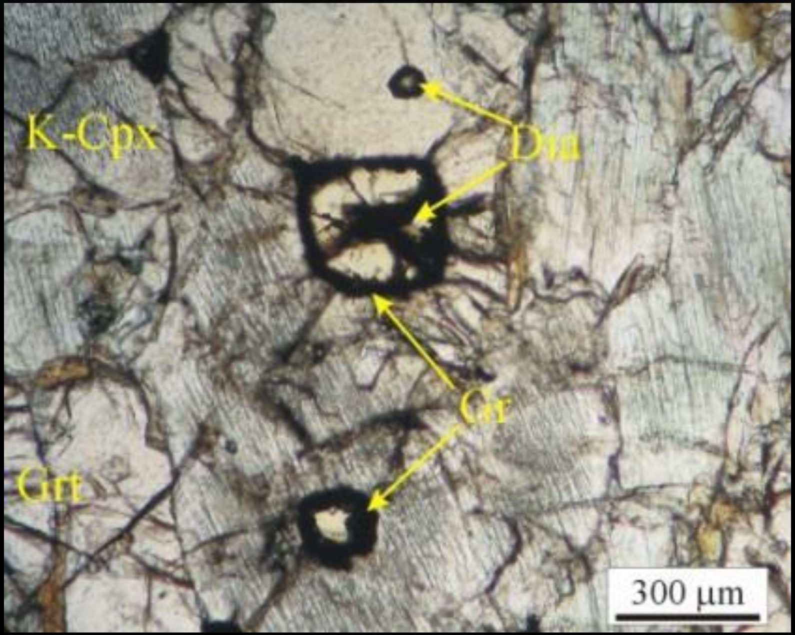


Figure 2. Photomicrographs. A: Graphite clusters. B: Polishing scratches from diamonds protruding from garnet. A–C, E: Identified diamonds in garnet. D: Identified diamond in kyanite. A, C, and D are from felsic granulite, T-7 borehole. B and E are from intermediate granulites from Eger Crystalline Complex and from T-38 borehole. A–C were taken in reflected light; D and E were taken in transmitted light.

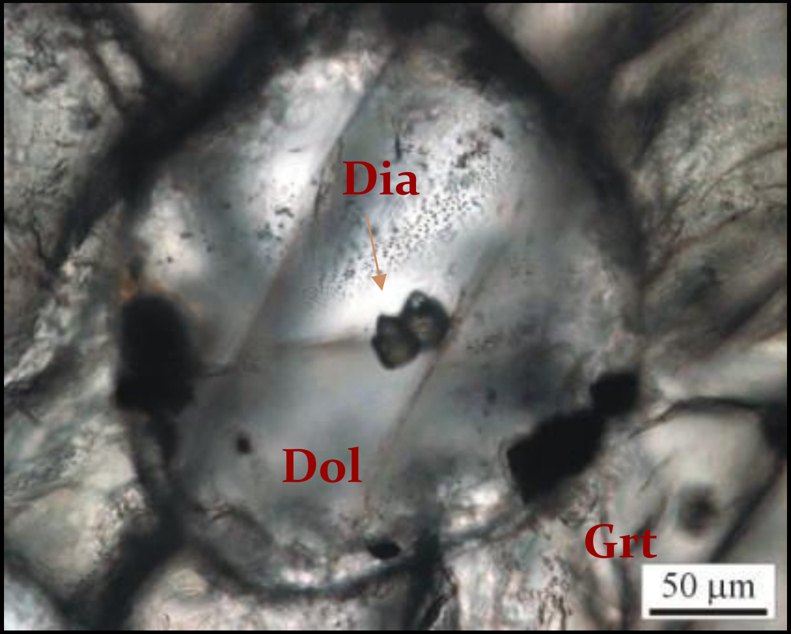
Diamond

Kokchetav Massif, Kazakhstan



Diamonds inclusions in clinopyroxene and garnet,

Kumdy Kol deposit



Diamonds inclusions in dolomite included in garnet,

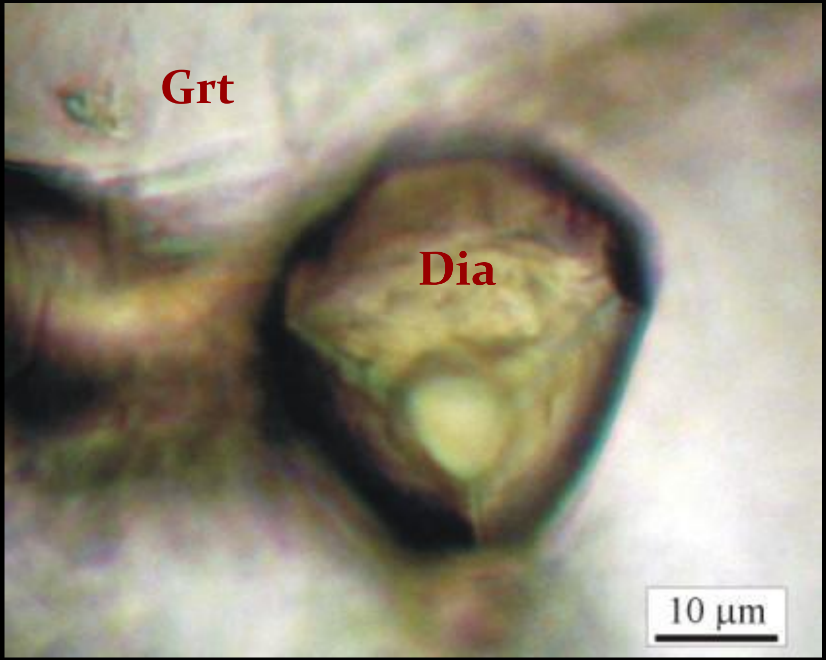
Kumdy Kol deposit

(Maria Perraki, Andrey Korsakov, David Smith, Evripidis Mposkos 2009, American Mineralogist, 94, 546-556)

Diamond
Kokchetav Massif, Kazakhstan

Matrix Diamonds,

Kumdy-Kol deposit

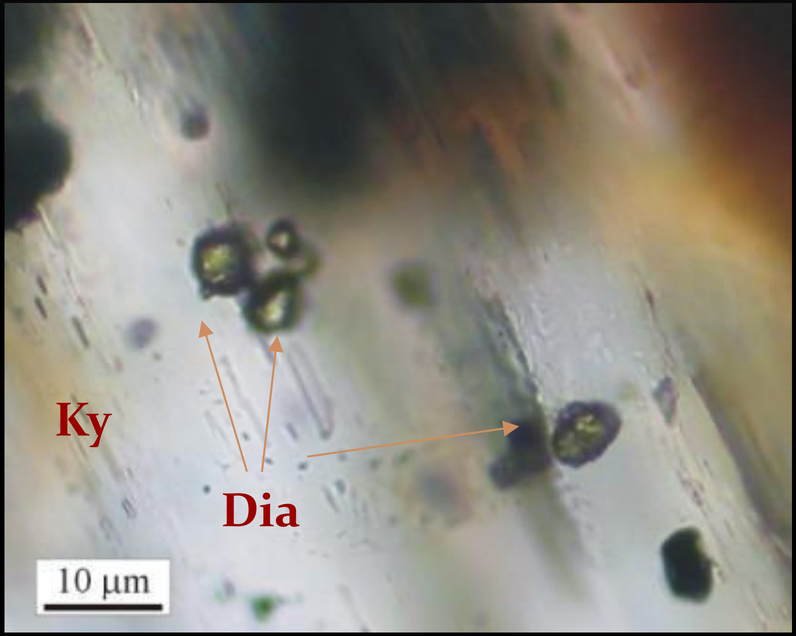


Diamond inclusion in garnet,

Barchi-Kol deposit

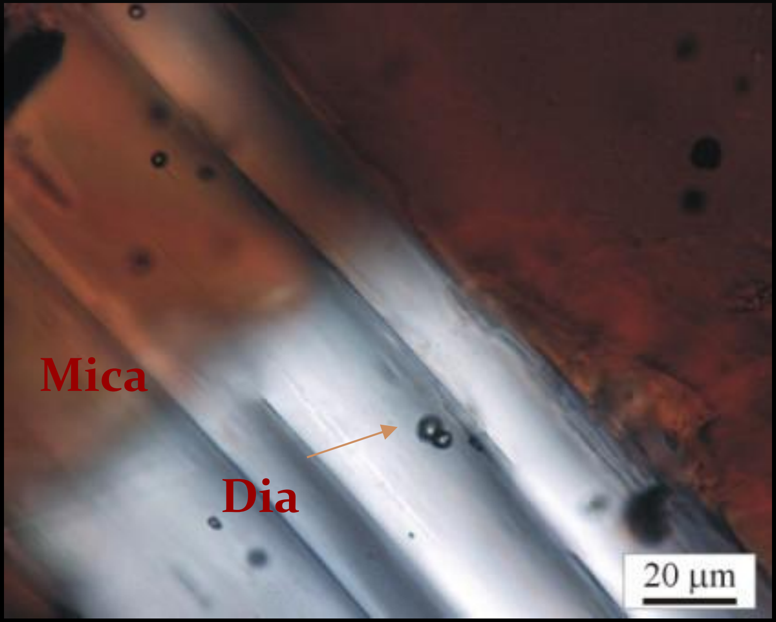
(Maria Perraki, Andrey Korsakov, David Smith, Evripidis Mposkos 2009, American Mineralogist, 94, 546-556)

Diamond
Kokchetav Massif, Kazakhstan



Diamonds inclusions in kyanite,

Barchi Kol deposit



Diamonds inclusions in mica,

Barchi Kol deposit

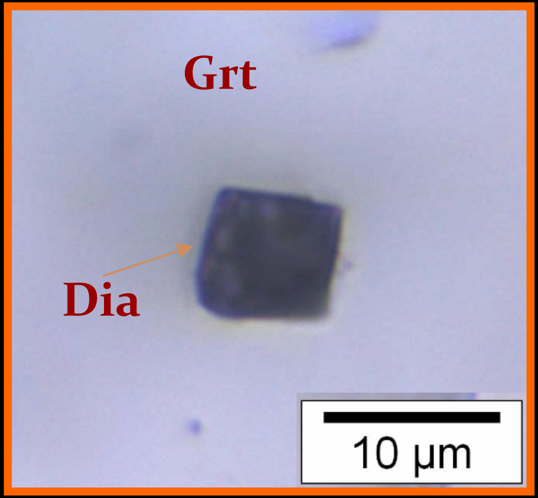
(Maria Perraki, Andrey Korsakov, David Smith, Evripidis Mposkos 2009, American Mineralogist, 94, 546-556)

Diamond
Erzgebirge Massif, Germany

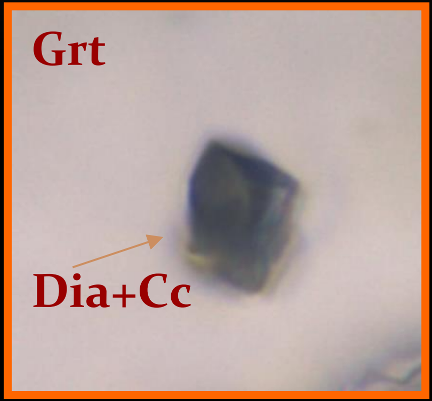
Diamond: Single inclusions or part of polyphase solid-melt inclusions in zircons or garnet from grt-ky-quartzofeldspathic rocks

(polyphase diamond-bearing inclusion first described in grt by Stoeckhert et al 2001, Geology, 391-394)

Diamond
Rhodope Metamorphic Province, Greece



(Maria Perraki, Alexander Proyer, Evripidis Mposkos, Reinhard Kaindl, Georg Hoinkes, 2006, EPSL, 241, 672-685)

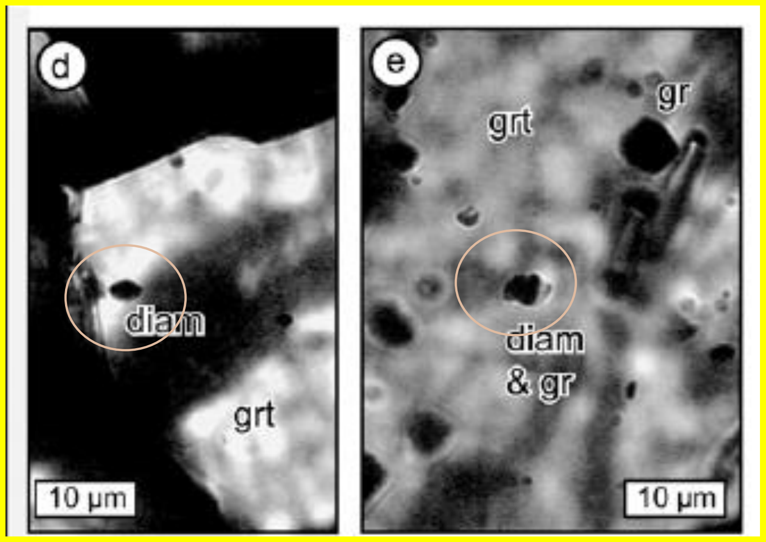


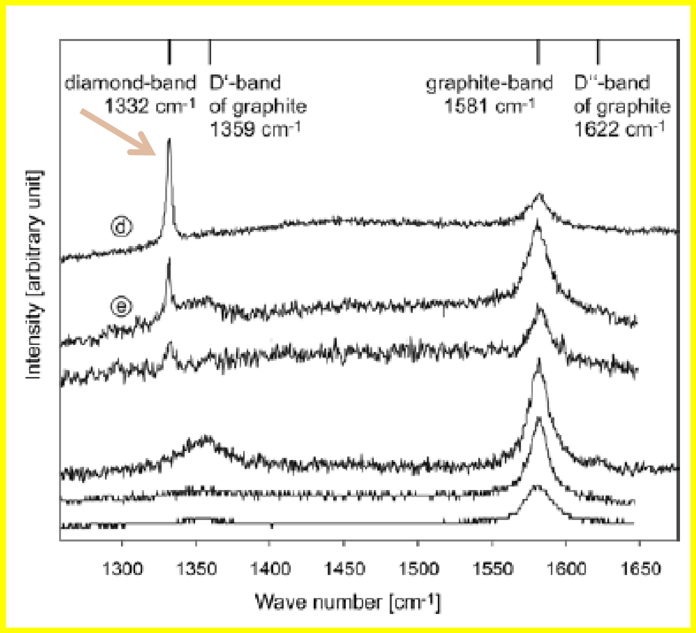
Eur. J. Mineral.
Fast Track DOI: 10.1127/0935-1221/2010/0022-1999

Fast Track Article

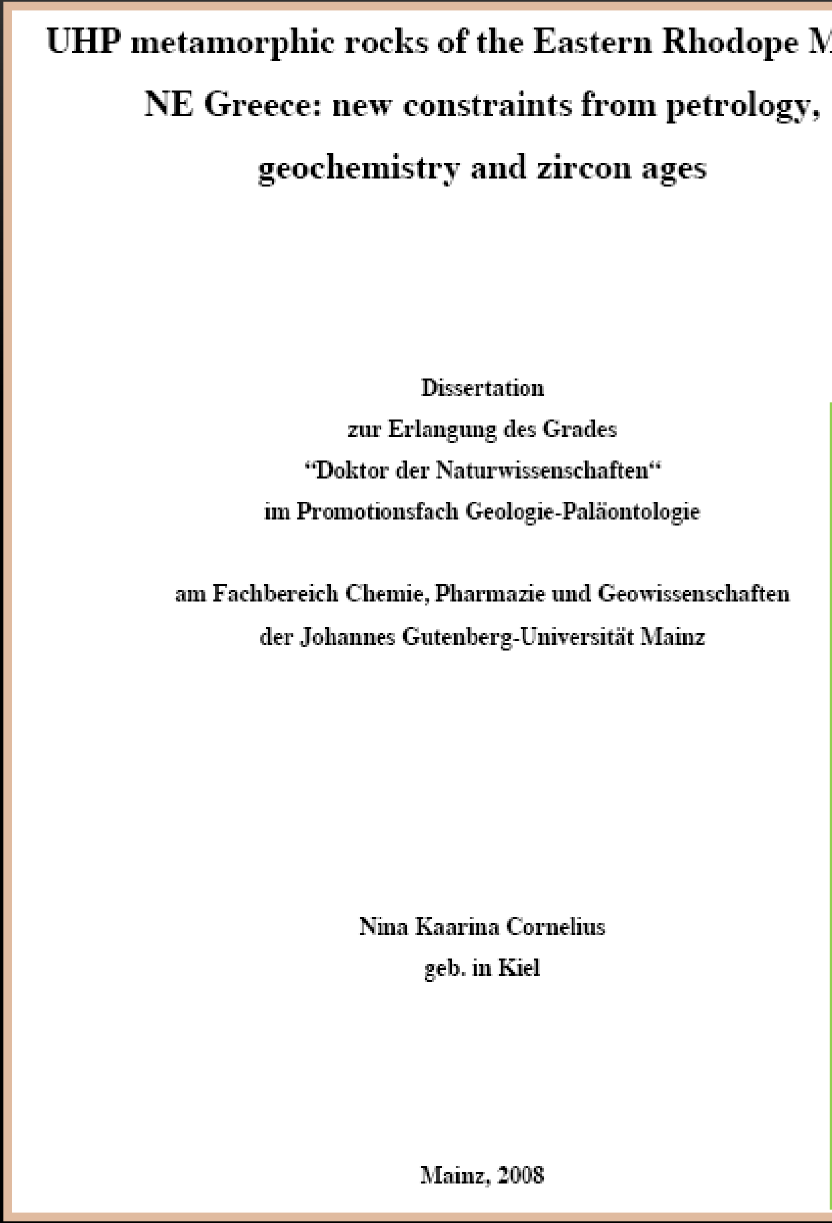
A new occurrence of microdiamond-bearing metamorphic rock, SW Rhodopes, Greece

SILKE SCHMIDT[1,*], THORSTEN J. NAGEL[2] and NIKOLAUS FROITZHEIM[2]





pseudosections.



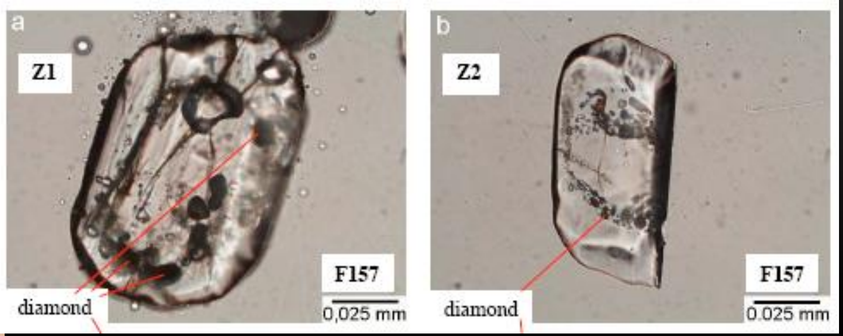
UHP metamorphic rocks of the Eastern Rhodope Massif, NE Greece: new constraints from petrology, geochemistry and zircon ages

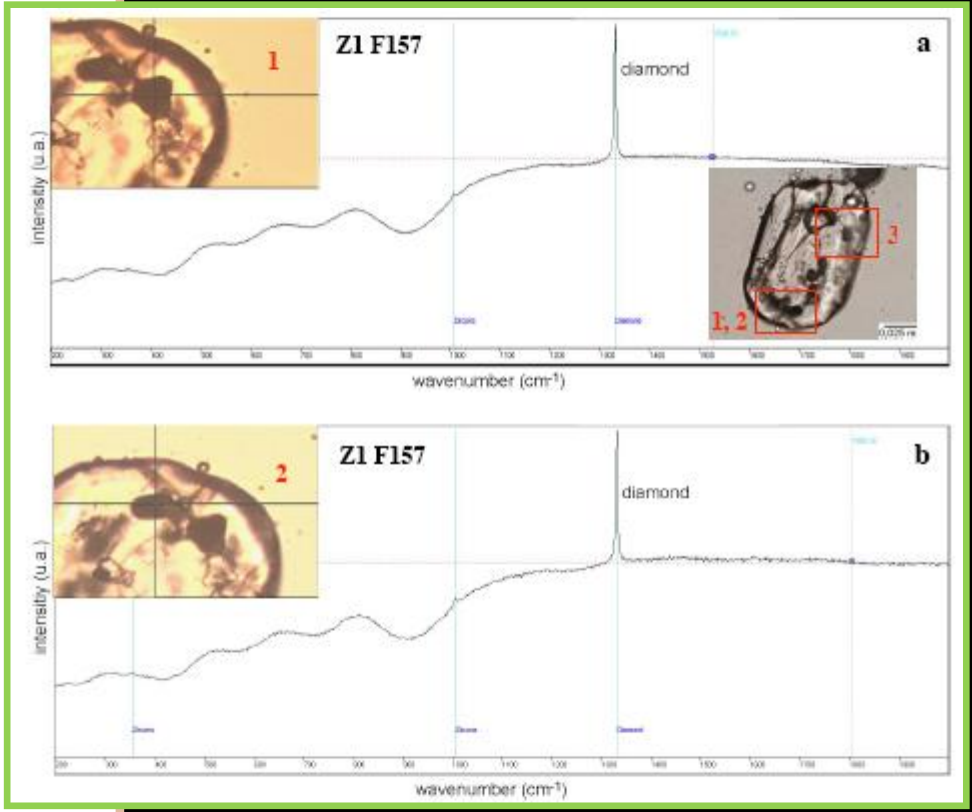
Dissertation
zur Erlangung des Grades
“Doktor der Naturwissenschaften“
im Promotionsfach Geologie-Paläontologie

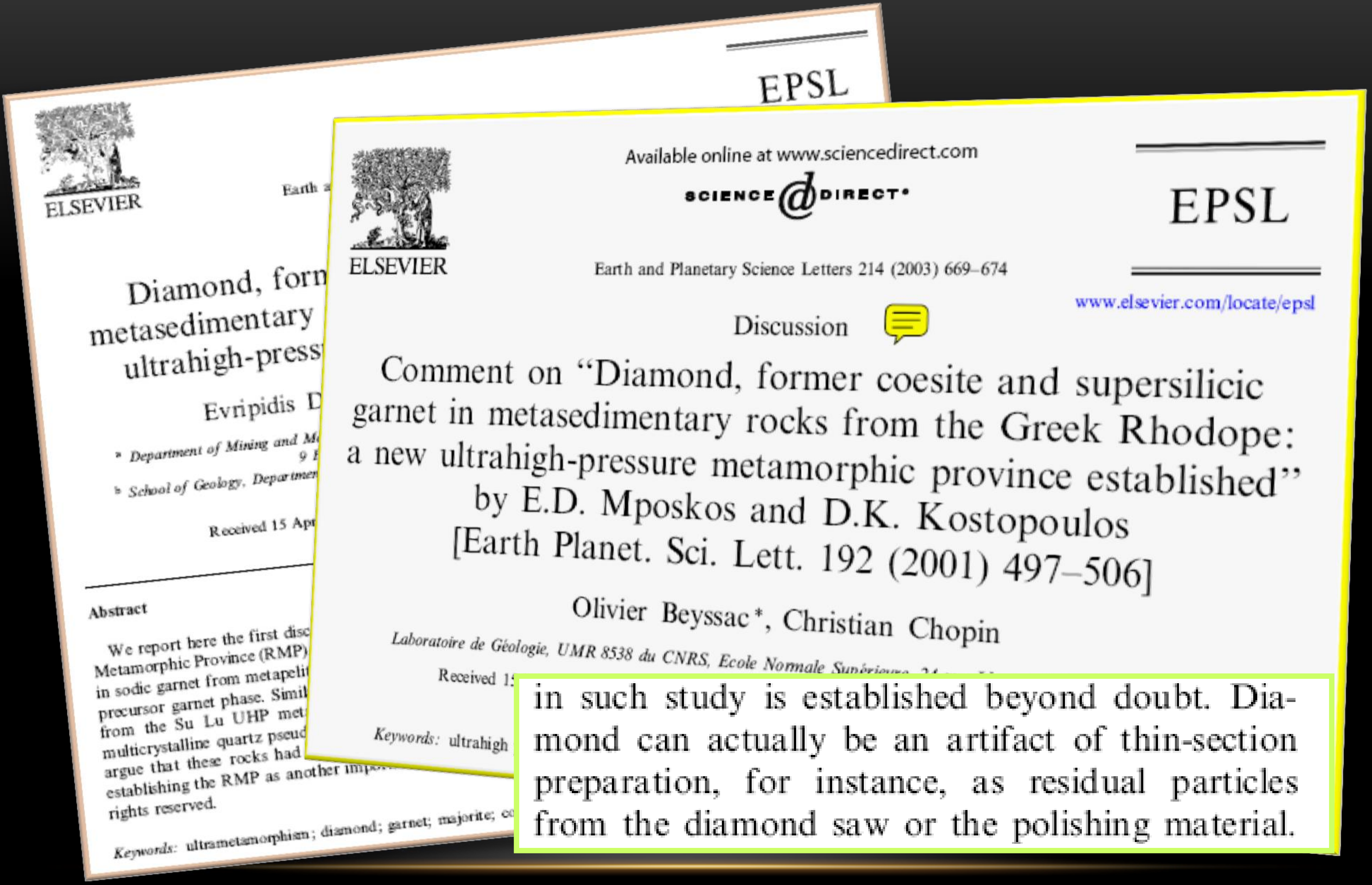
am Fachbereich Chemie, Pharmazie und Geowissenschaften
der Johannes Gutenberg-Universität Mainz

Nina Kaarina Cornelius
geb. in Kiel

Mainz, 2008







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Earth a

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Diamond, forn
metasedimentary
ultrahigh-press

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ᵃ Department of Mining and M
9 E

ᵇ School of Geology, Departmen

Received 15 Apr

Abstract

We report here the first disc
Metamorphic Province (RMP)
in sodic garnet from metapelit
precursor garnet phase. Simil
from the Su Lu UHP met
multicrystalline quartz pseud
argue that these rocks had
establishing the RMP as another impo
rights reserved.

Keywords: ultrametamorphism; diamond; garnet; majorite; co

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Earth and Planetary Science Letters 214 (2003) 669–674

EPSL

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Discussion

Comment on "Diamond, former coesite and supersilicic garnet in metasedimentary rocks from the Greek Rhodope: a new ultrahigh-pressure metamorphic province established" by E.D. Mposkos and D.K. Kostopoulos [Earth Planet. Sci. Lett. 192 (2001) 497–506]

Olivier Beyssac*, Christian Chopin

Laboratoire de Géologie, UMR 8538 du CNRS, Ecole Normale Supérieure

Received 1

Keywords: ultrahigh

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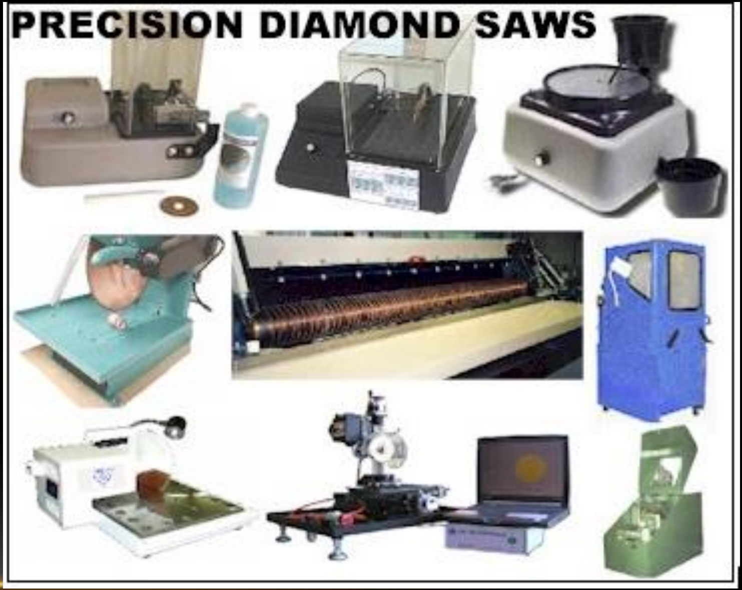
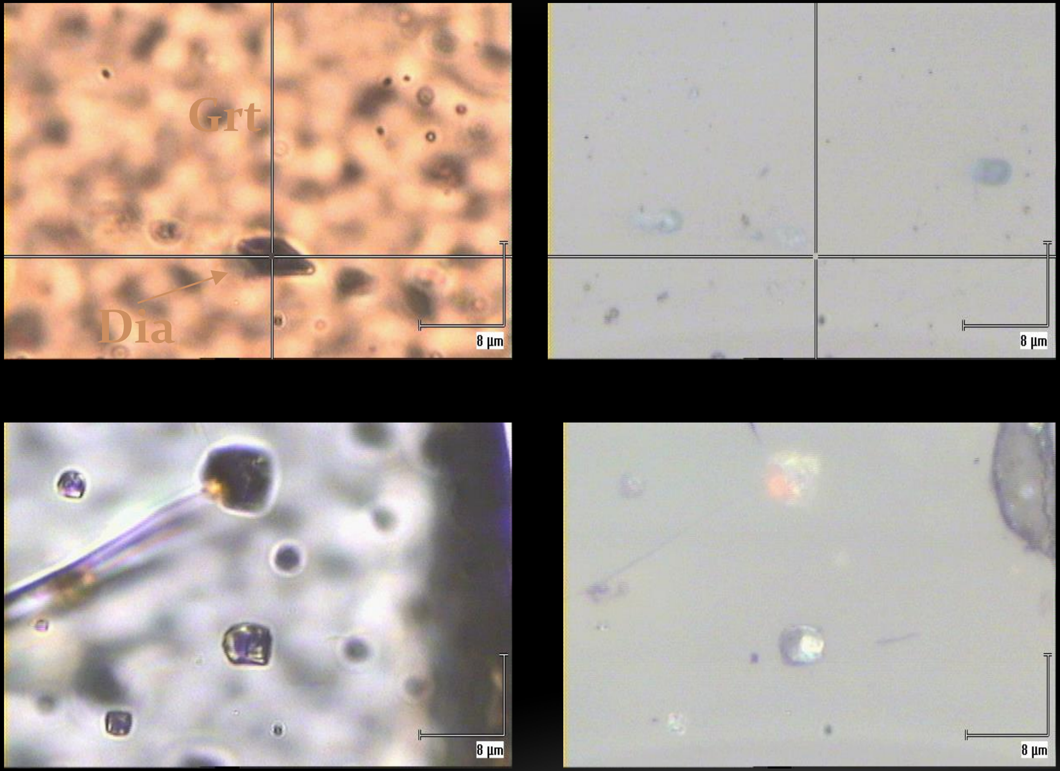
in such study is established beyond doubt. Diamond can actually be an artifact of thin-section preparation, for instance, as residual particles from the diamond saw or the polishing material.

Diamond polishing materials
Diamond cutting saws



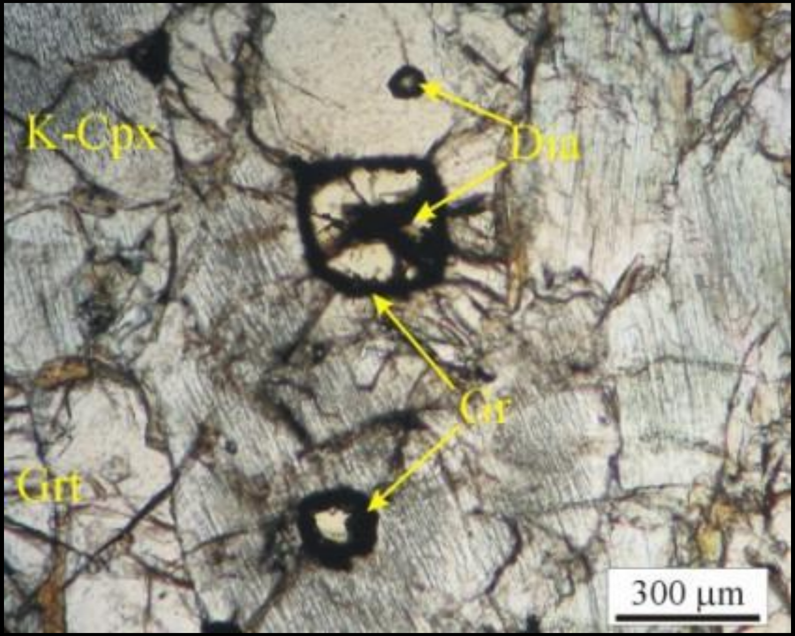
Thin section surface



✓ ☺

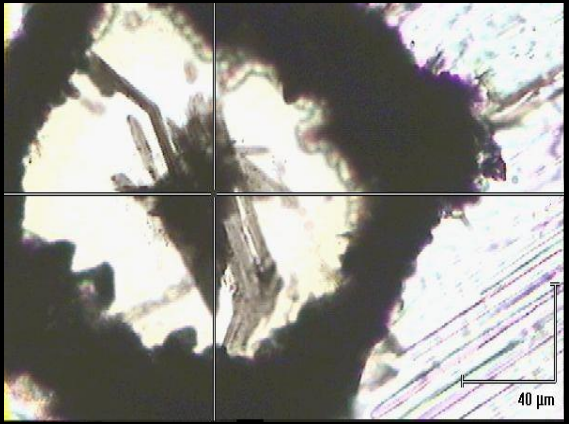
? 😐

Diamond size



>>> polishing diamond size → ✓ ☺

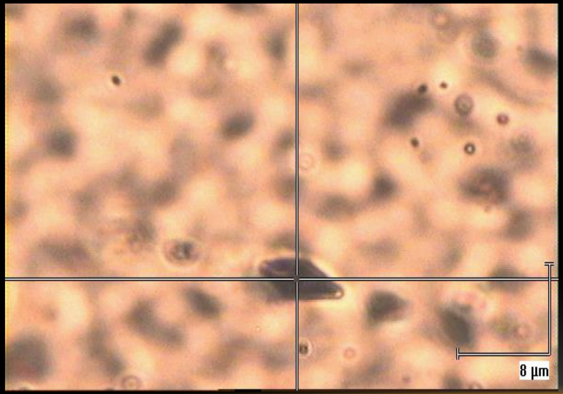
Inclusions/coatings/ coexistent phases



Graphite inclusion in and graphite coating around diamond

(Kokchetav Massif, Kazakhstan)

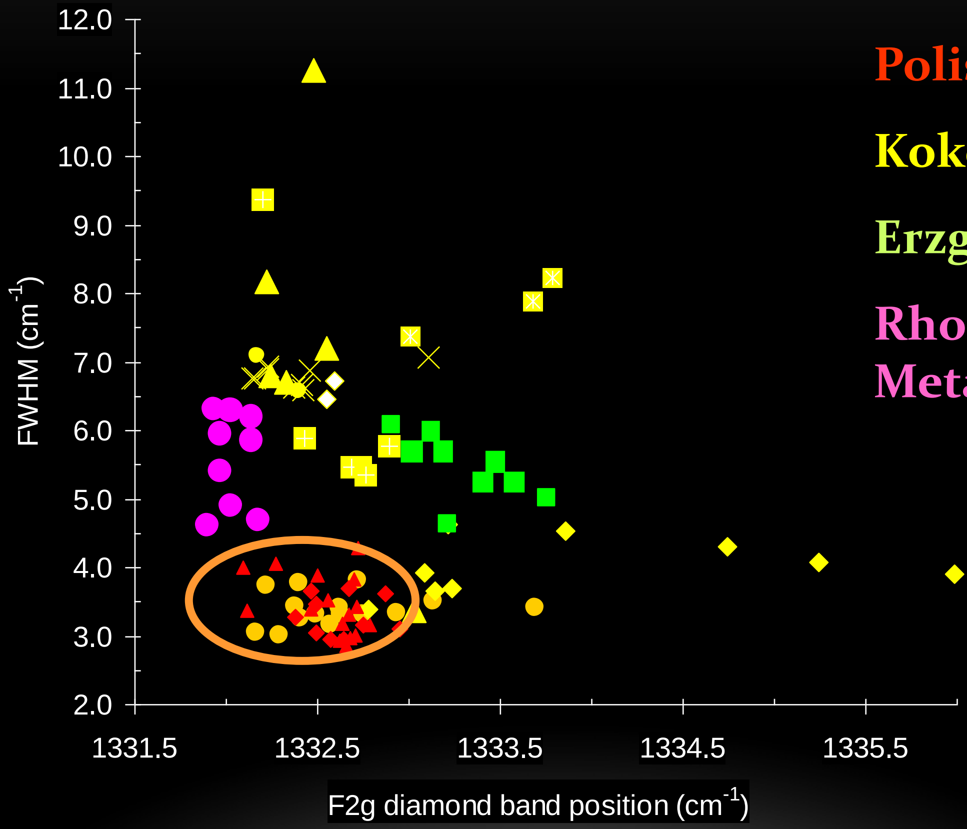
✓☺



Diamond + CO_2 + carbonate

(Rhodope Metamorphic Province, Greece)

Diamond Raman Spectra



Polishing materials

Kokchetav Massif

Erzgebirge Massif

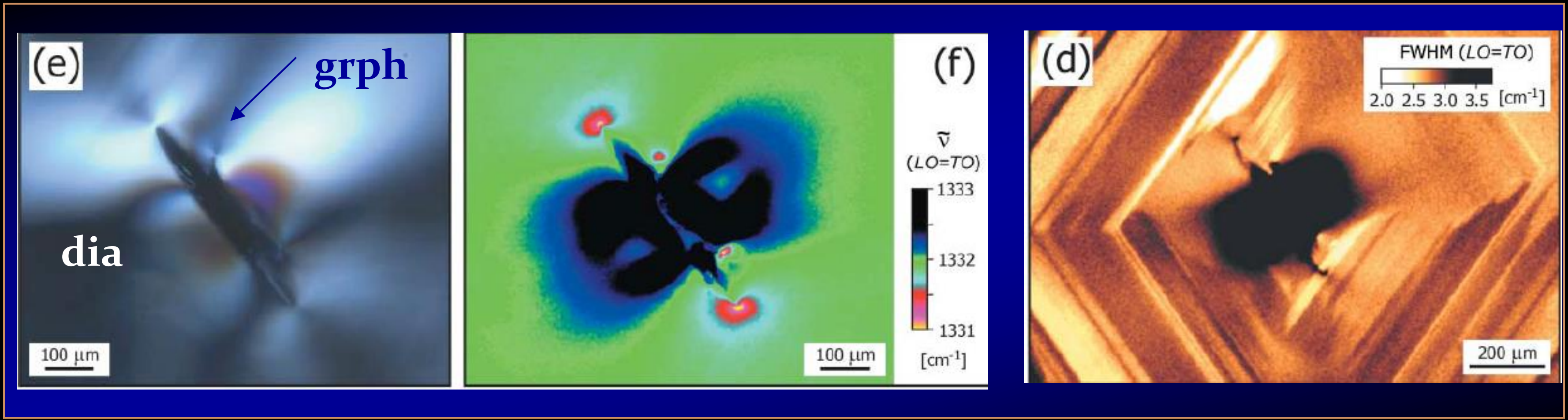
Rhodope Metamorphic Province

F2g diamond band: Shift & broadening

- Increasing laser power / heating (e.g. Zhao et al. 1998)
- Decreasing of particle size (nanoparticles, e.g. Yoshikawa et al. 1995)
- **Internal stress variations (e.g. Grimsditch et al. 1978)**
- **Nitrogen (or B, or...) impurities (e.g. Surovtsev et al. 1999)**
- Metamictization of diamond by zircon's radioactive content (e.g. Godard et al. 2004)

F2g diamond band: Shift & broadening Internal stress variations

A. Internal stress caused by inclusions in diamonds due to different elastic properties between the diamond and the inclusion



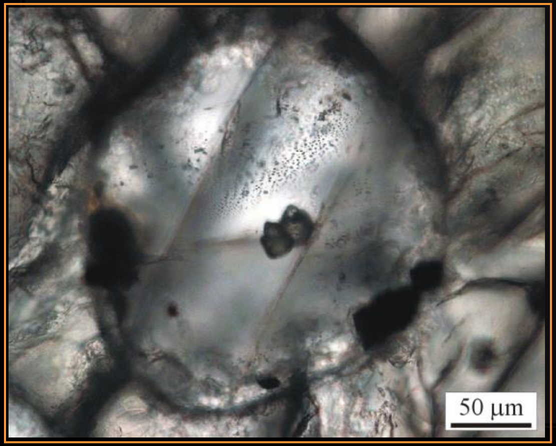
Diamond with single-crystal of graphite inclusion from the Panda Kimberlite, Canada

Nasdala et al. 2005, American Mineralogist, 90, 747-748

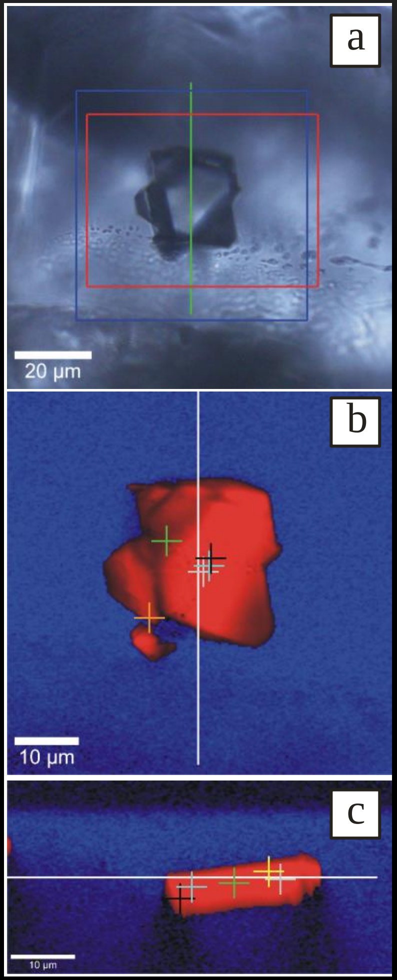
F2g diamond band: Shift & broadening Internal stress variations

B. Remained overpressure in diamond inclusions in robust minerals (e.g. garnet, zircon) caused by different elastic properties between the diamond inclusion and the host mineral

very possible in the case of UHP metamorphic rocks



DIAMOND FROM UHPM ROCKS



Diamond inclusion in garnet (a) and Raman maps and the depth scan were performed in the area marked in blue and green line respectively

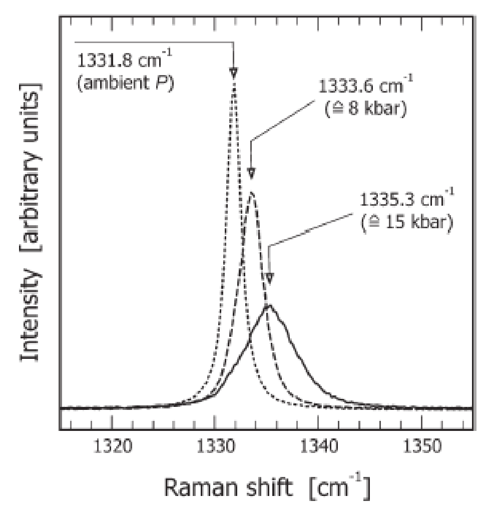
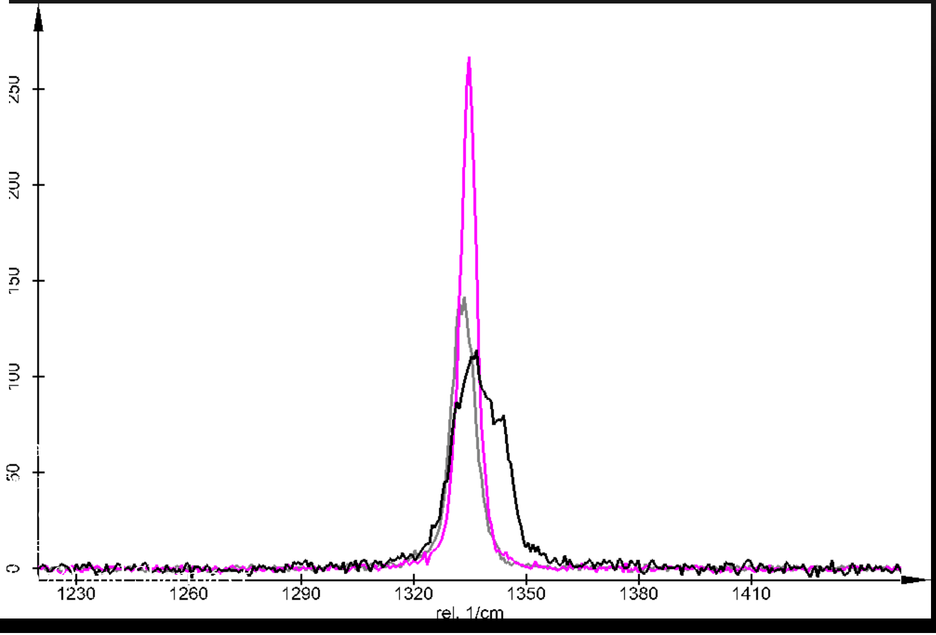
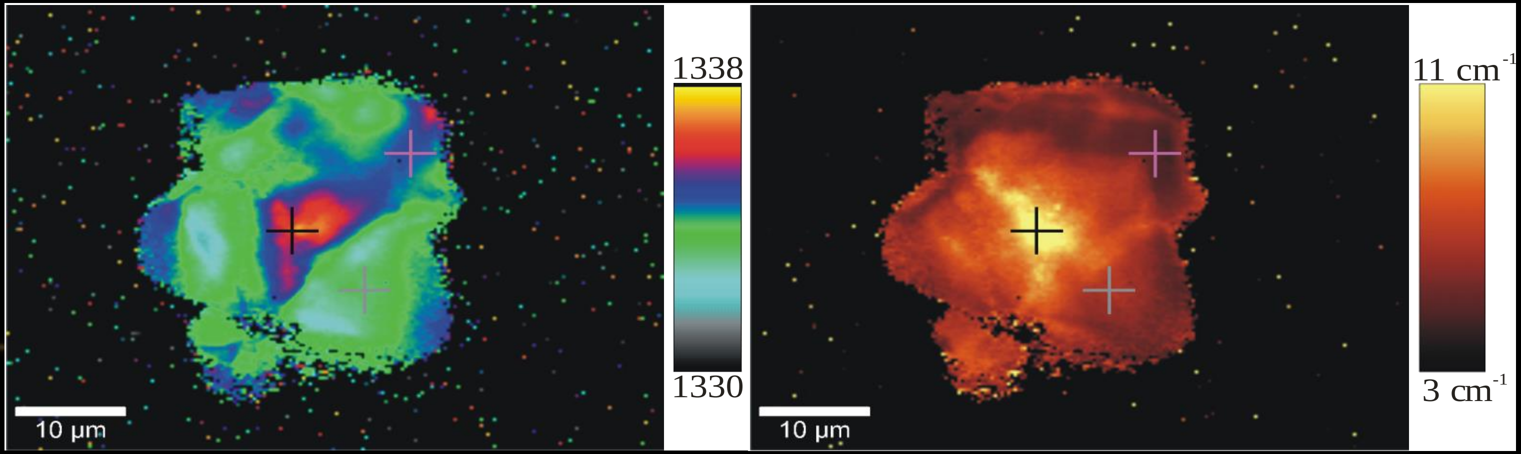


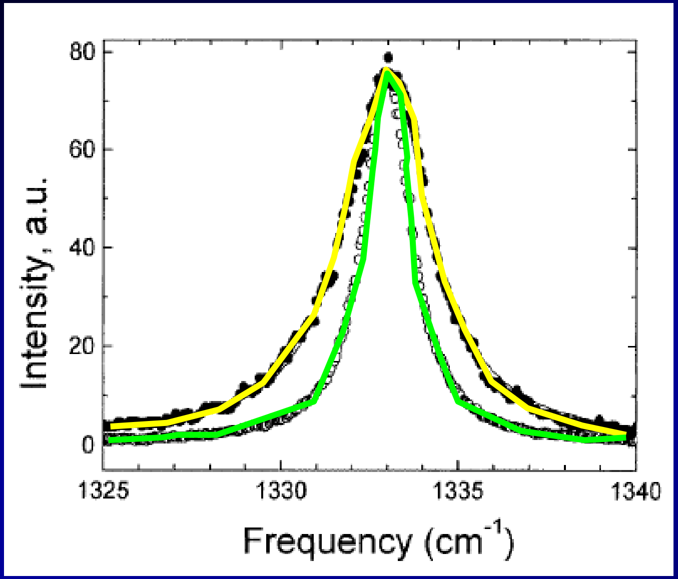
FIGURE 1. Raman spectra of three micro-ar
inside diamond specimen PAG12. Increased
(compressive strain) is indicated by the incr
the diamond *LO*=*TO* phonon. Remnant pre
based on the calibrations of Grimsditch et a
al. (1985). (Nasdala et al., 2005)

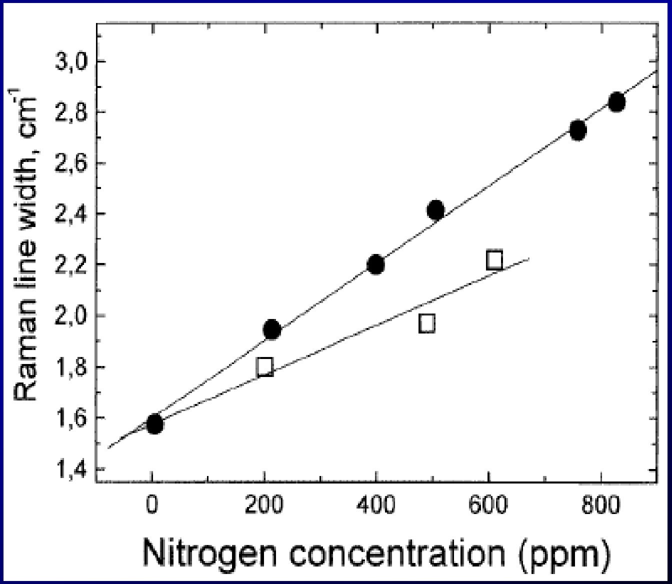




The results of the Lorenzian curve fits for exact position and the width are displayed in the images left and right

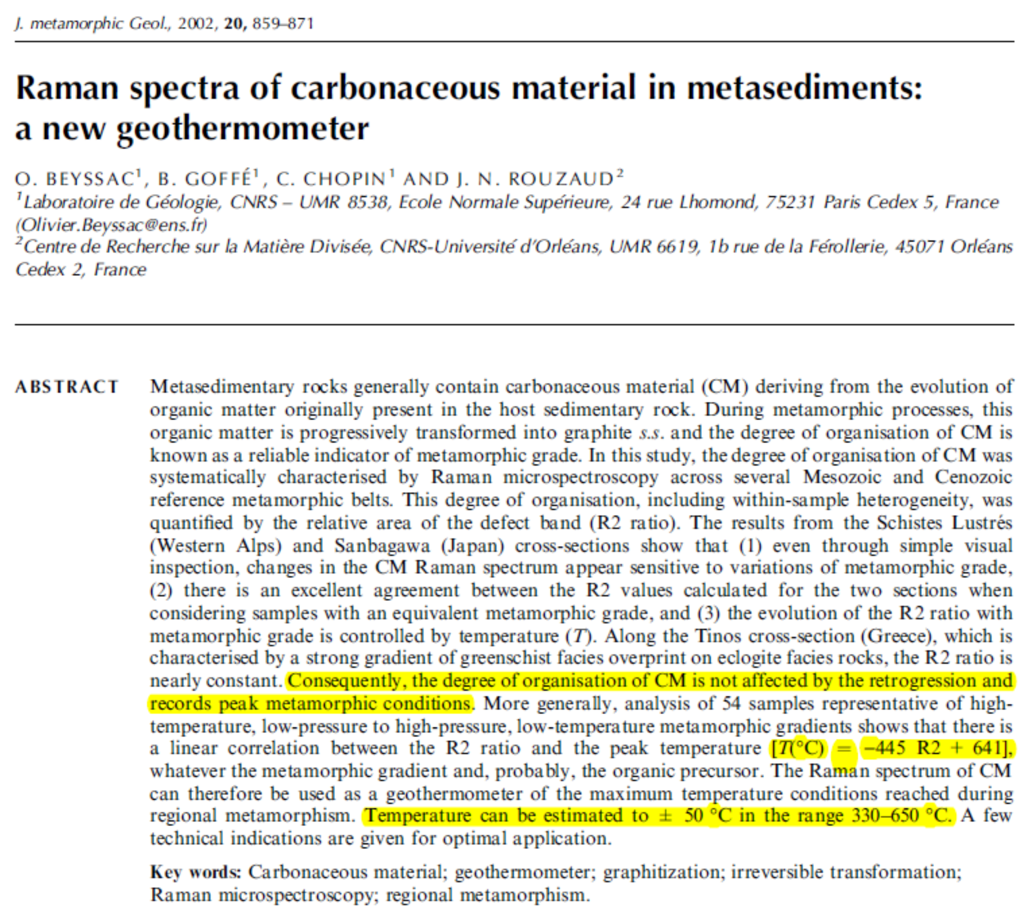
F2g diamond band: Shift & broadening (Nitrogen) impurities





Surovtsev et al. 1999, J. Phys.: Condens. Matter 11 (1999) 4767–4774

Graphite ordered-disordered



J. metamorphic Geol., 2002, **20**, 859–871

Raman spectra of carbonaceous material in metasediments: a new geothermometer

O. BEYSSAC[1], B. GOFFÉ[1], C. CHOPIN[1] AND J. N. ROUZAUD[2]

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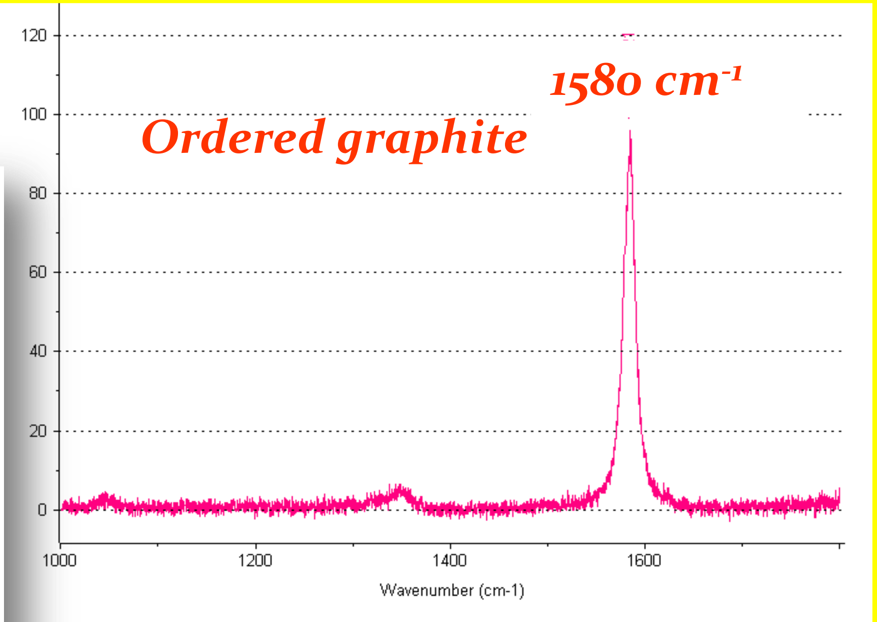
[2]Centre de Recherche sur la Matière Divisée, CNRS-Université d'Orléans, UMR 6619, 1b rue de la Férollerie, 45071 Orléans Cedex 2, France

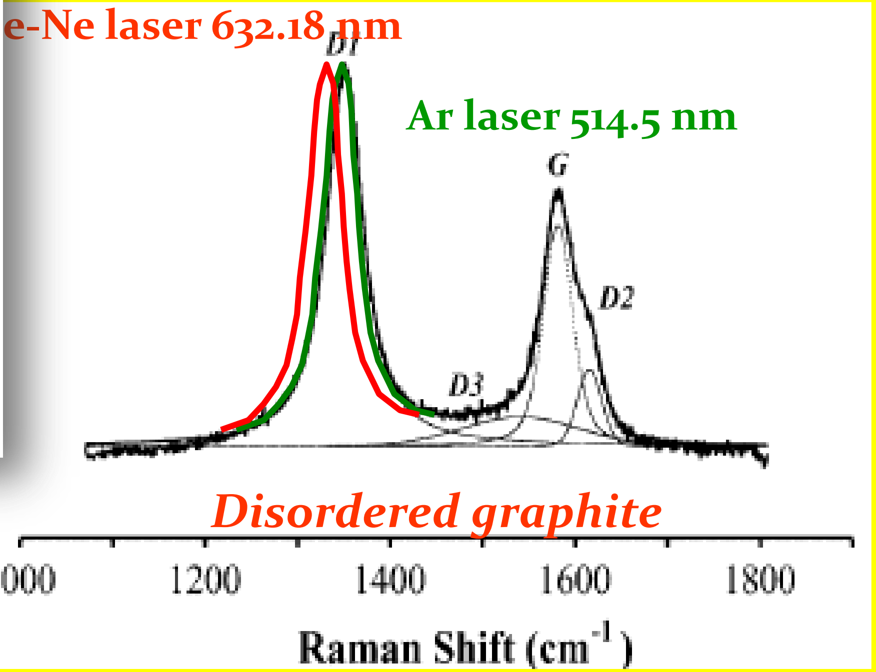
ABSTRACT Metasedimentary rocks generally contain carbonaceous material (CM) deriving from the evolution of organic matter originally present in the host sedimentary rock. During metamorphic processes, this organic matter is progressively transformed into graphite *s.s.* and the degree of organisation of CM is known as a reliable indicator of metamorphic grade. In this study, the degree of organisation of CM was systematically characterised by Raman microspectroscopy across several Mesozoic and Cenozoic reference metamorphic belts. This degree of organisation, including within-sample heterogeneity, was quantified by the relative area of the defect band (R2 ratio). The results from the Schistes Lustrés (Western Alps) and Sanbagawa (Japan) cross-sections show that (1) even through simple visual inspection, changes in the CM Raman spectrum appear sensitive to variations of metamorphic grade, (2) there is an excellent agreement between the R2 values calculated for the two sections when considering samples with an equivalent metamorphic grade, and (3) the evolution of the R2 ratio with metamorphic grade is controlled by temperature (*T*). Along the Tinos cross-section (Greece), which is characterised by a strong gradient of greenschist facies overprint on eclogite facies rocks, the R2 ratio is nearly constant. Consequently, the degree of organisation of CM is not affected by the retrogression and records peak metamorphic conditions. More generally, analysis of 54 samples representative of high-temperature, low-pressure to high-pressure, low-temperature metamorphic gradients shows that there is a linear correlation between the R2 ratio and the peak temperature [*T*(°C) = −445 R2 + 641], whatever the metamorphic gradient and, probably, the organic precursor. The Raman spectrum of CM can therefore be used as a geothermometer of the maximum temperature conditions reached during regional metamorphism. Temperature can be estimated to ± 50 °C in the range 330–650 °C. A few technical indications are given for optimal application.

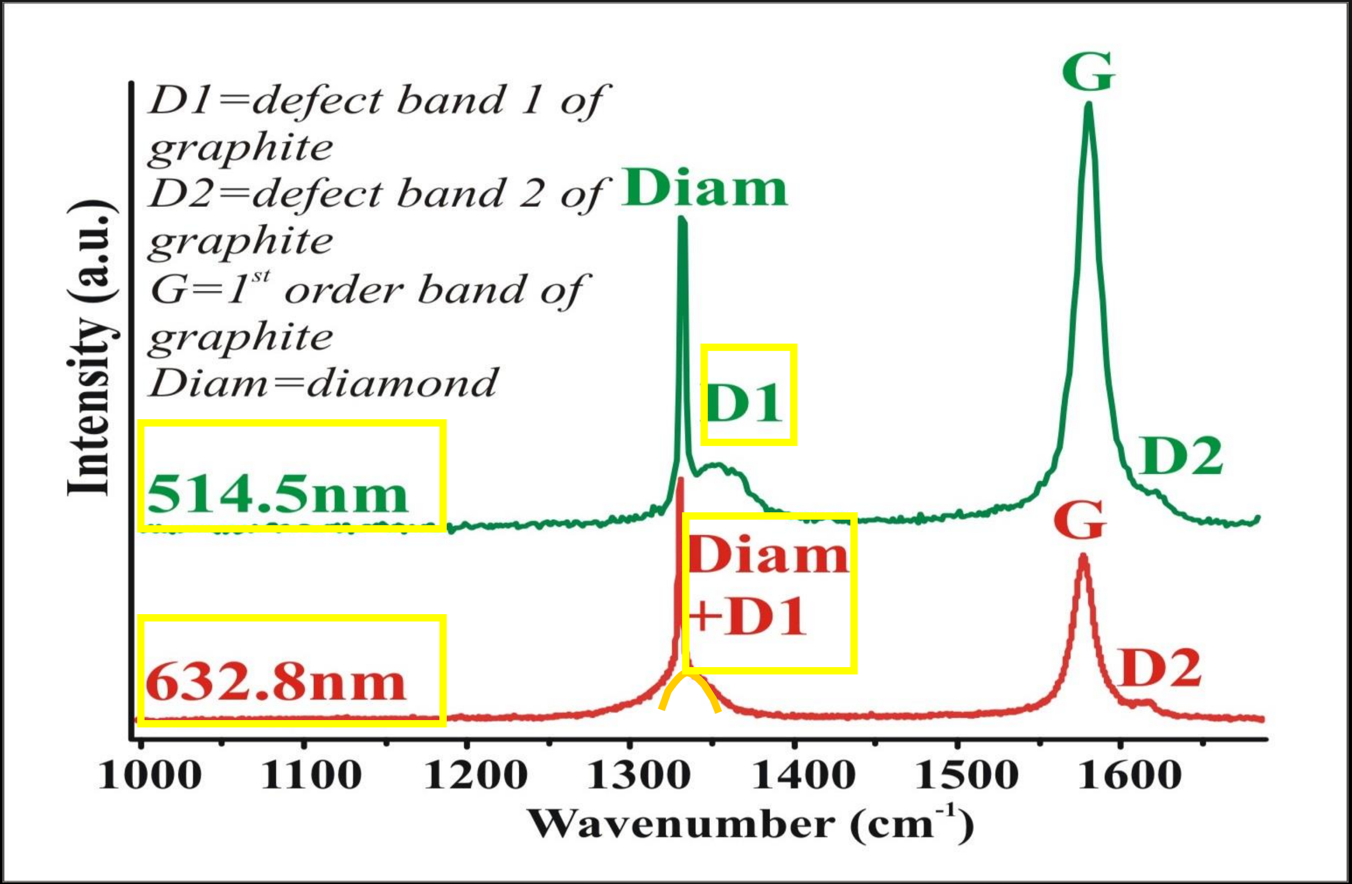
Key words: Carbonaceous material; geothermometer; graphitization; irreversible transformation; Raman microspectroscopy; regional metamorphism.

$$T\,(^{\circ}\mathrm{C}) = -445\mathrm{R2} + 641$$

R2= D1 / (G+D1+D2)





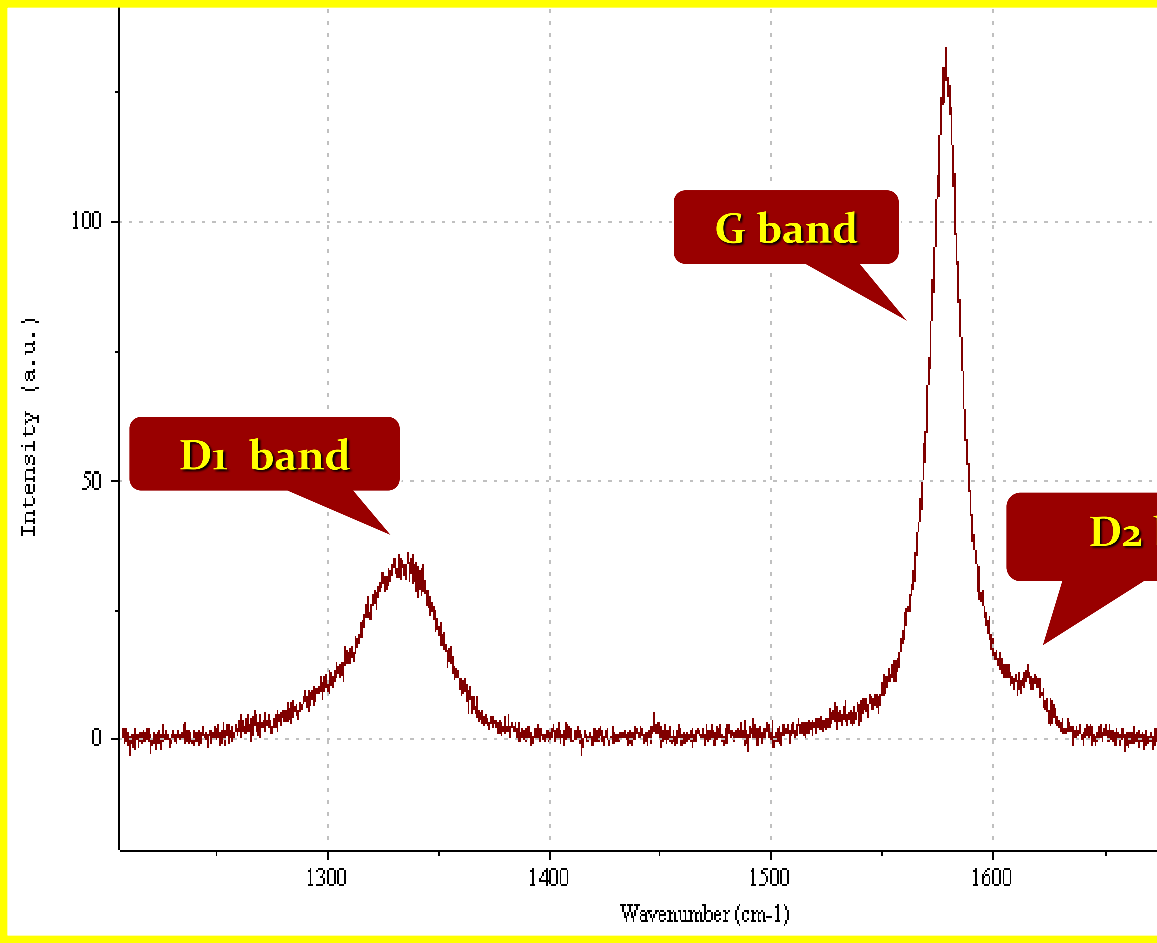


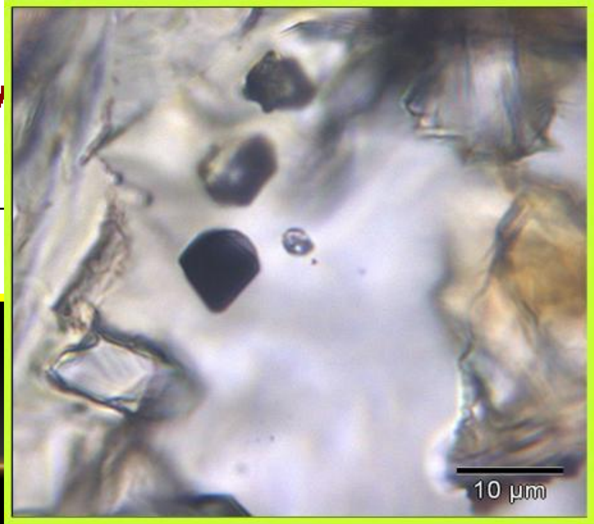
Diamond+graphite inclusion in garnet

(Greek Rhodope Metamorphic Province,

Perraki et al 2007, Spectrochimica Acta, 1077-1084

Cuboid disordered graphites





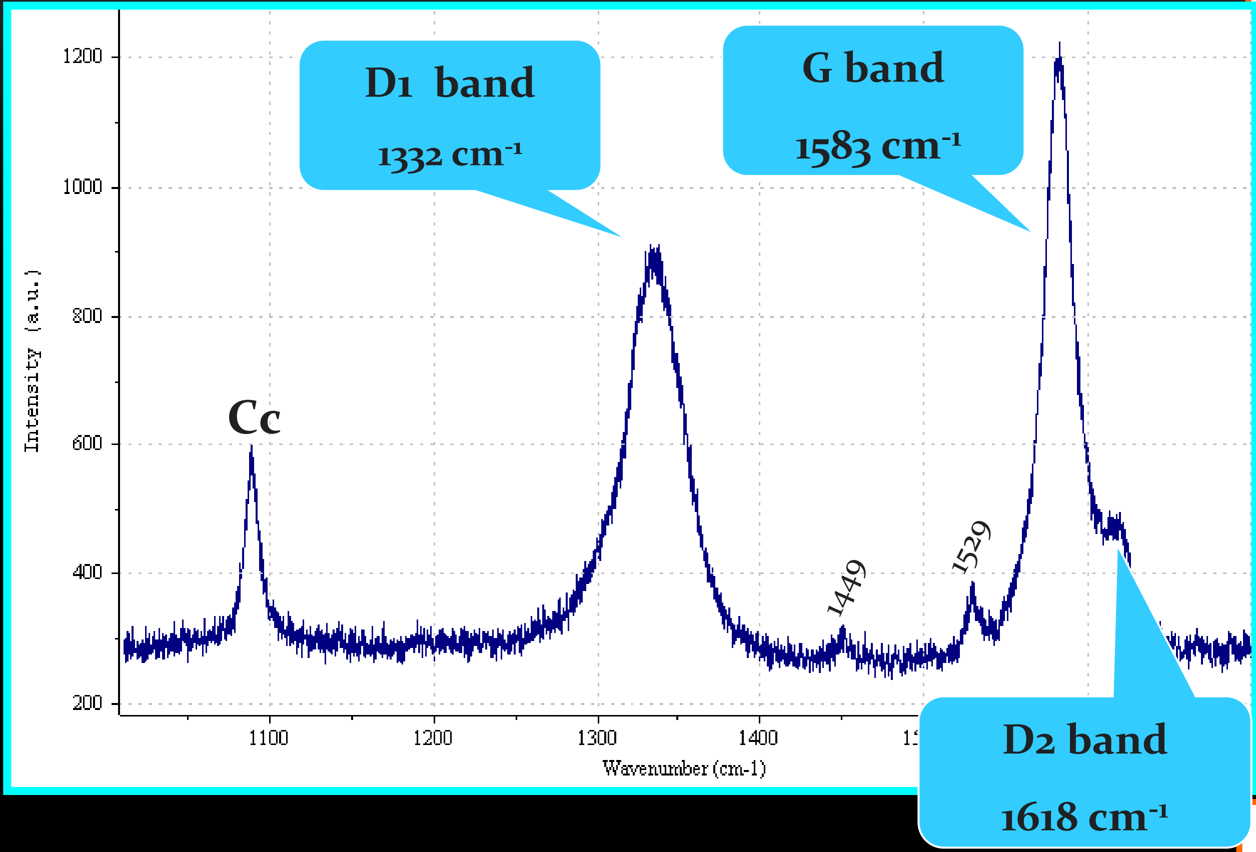
Order peak (G): 1578 cm^{-1}

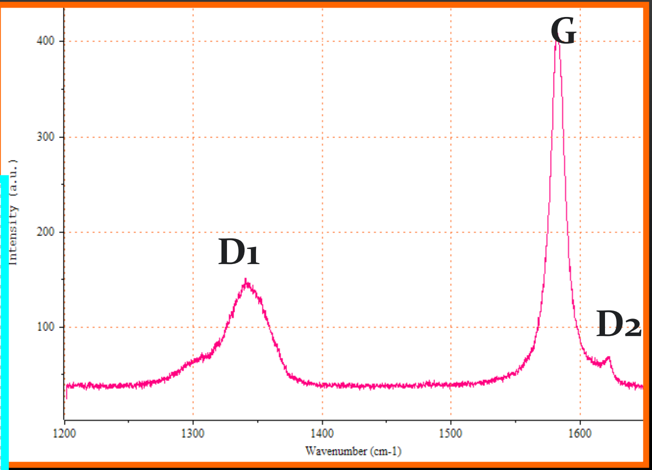
Disorder bands (D):

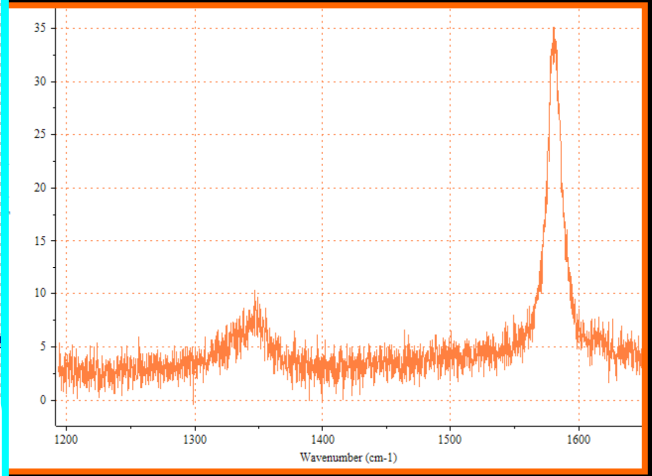
D1: 1330 cm^{-1}

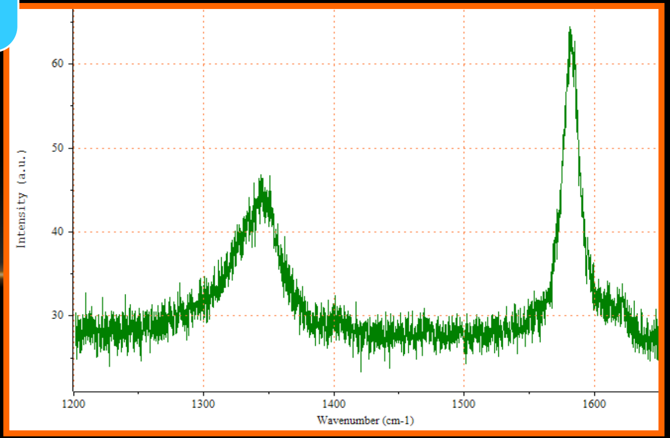
D2: 1617 cm^{-1}

Cuboid disordered graphites



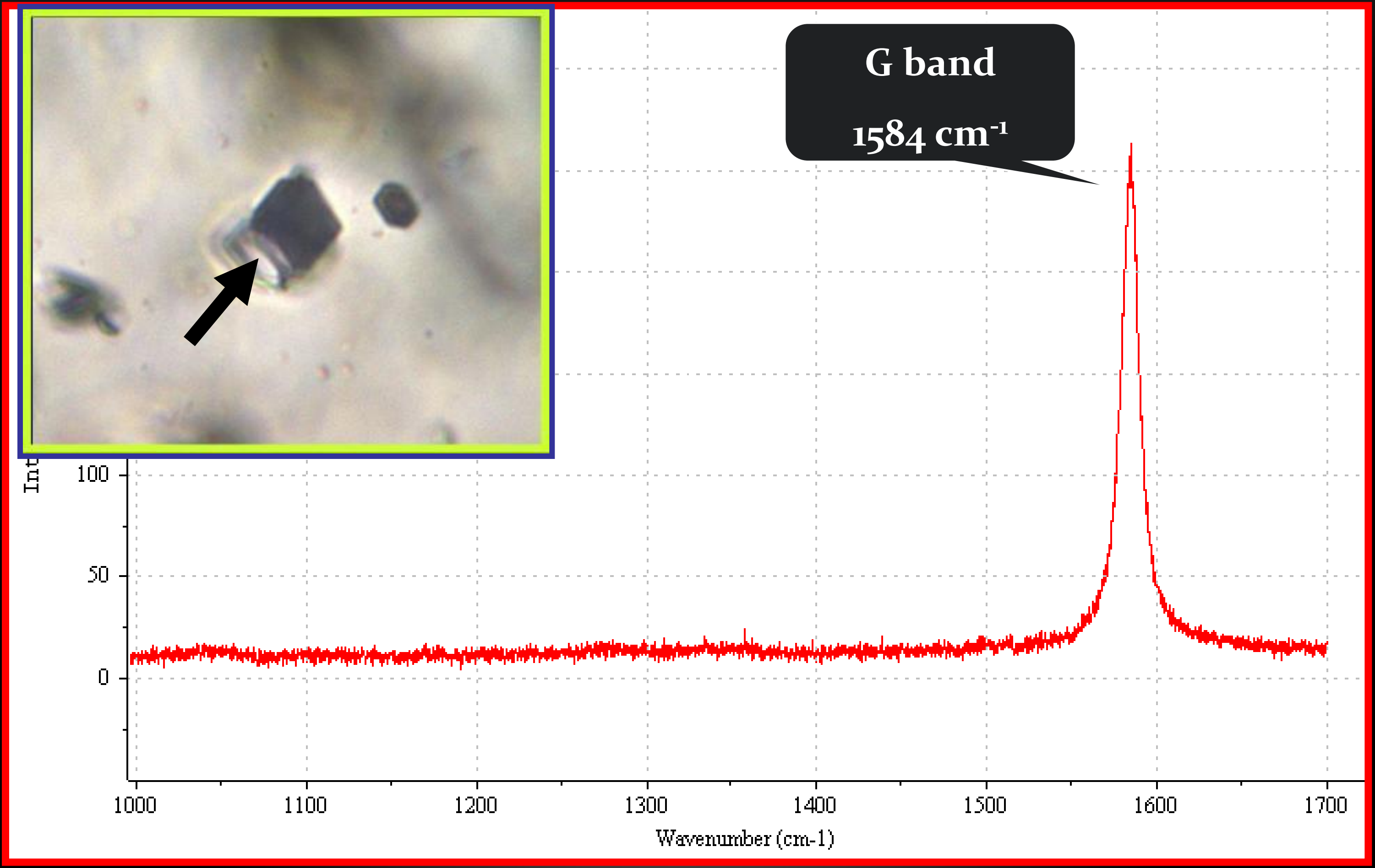


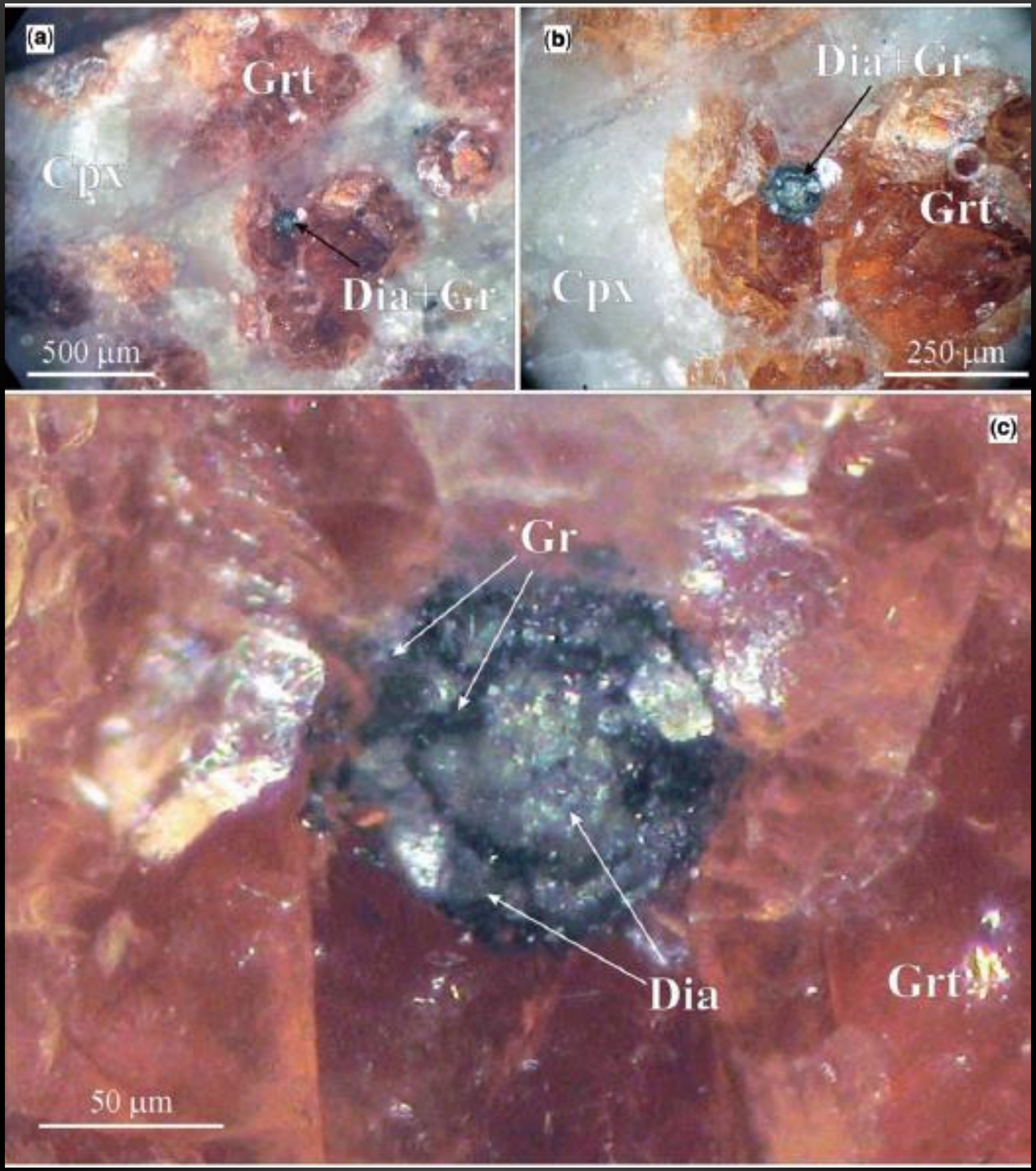




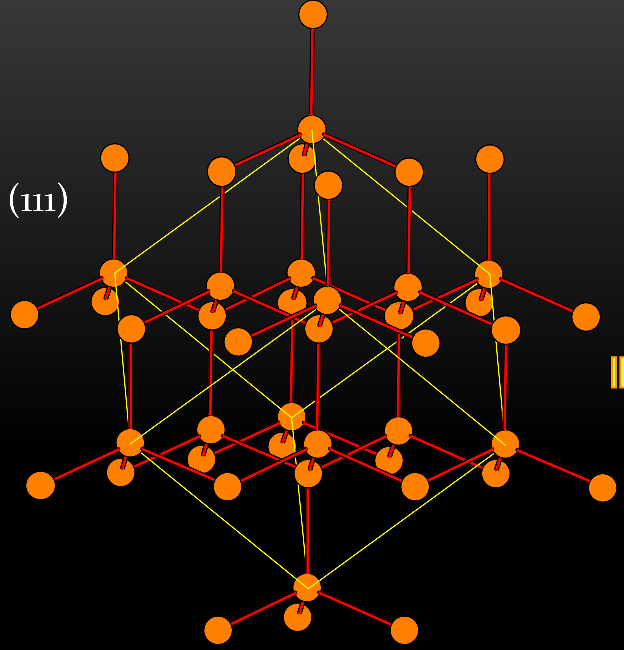
I_{D1}/I_G	0.26-0.86
$I_{D1}/(I_{D1}+I_G+I_{D3})$	0.20-0.42
Shift of D1 band	1330-1345

Highly ordered graphites

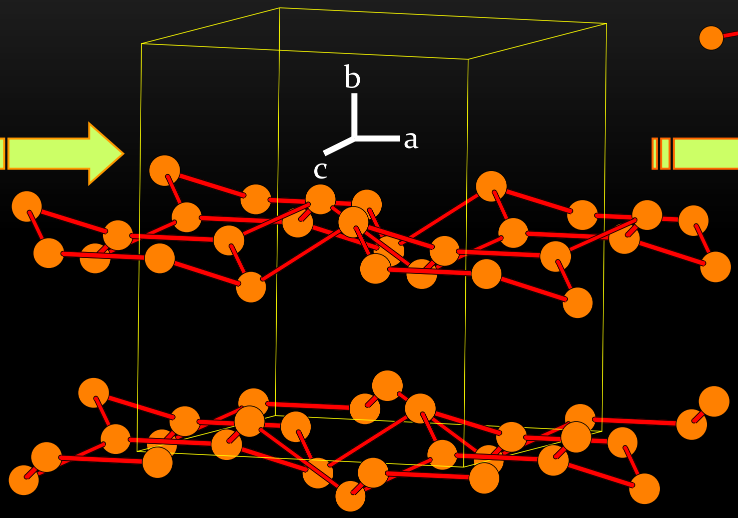


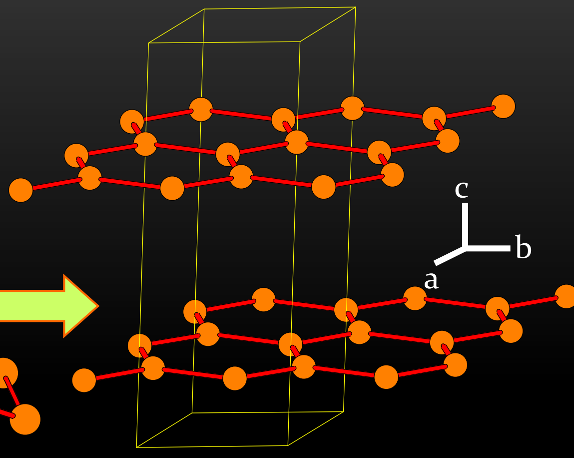


Diamond-graphite inclusion in garnet, Kokchetav Massif
Korsakov et al 2010, JoP, 763-788

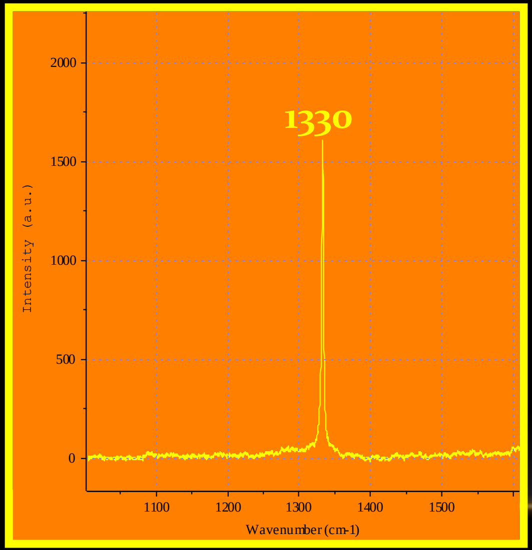


diamond

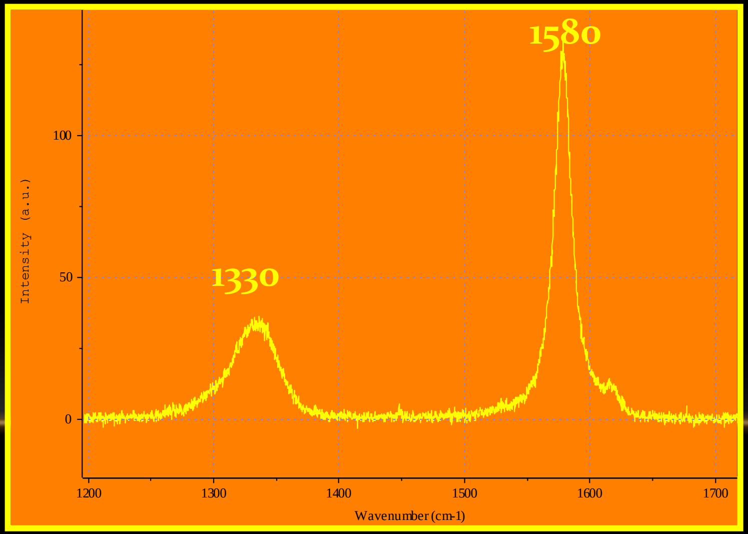


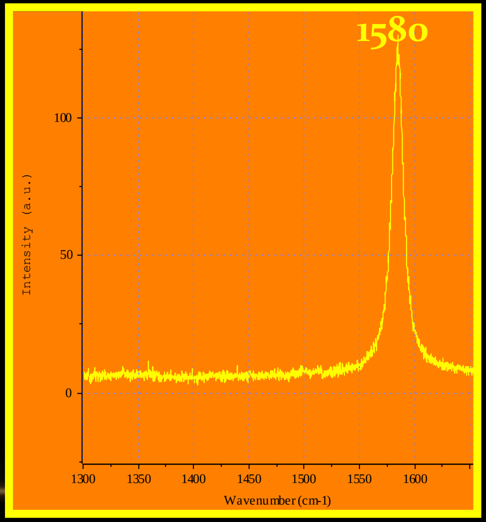


graphite



disordered graphite





(Crystal models from Inorganic Crystal Structure Database, 2004)

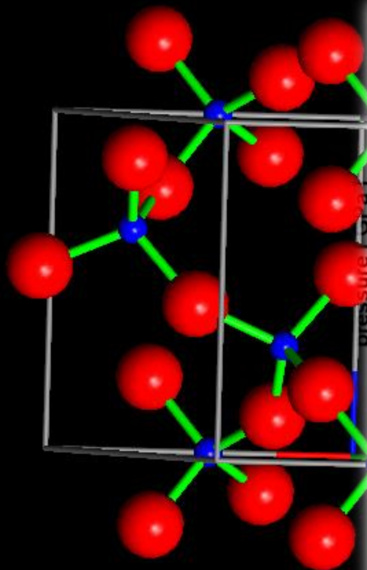
SiO2

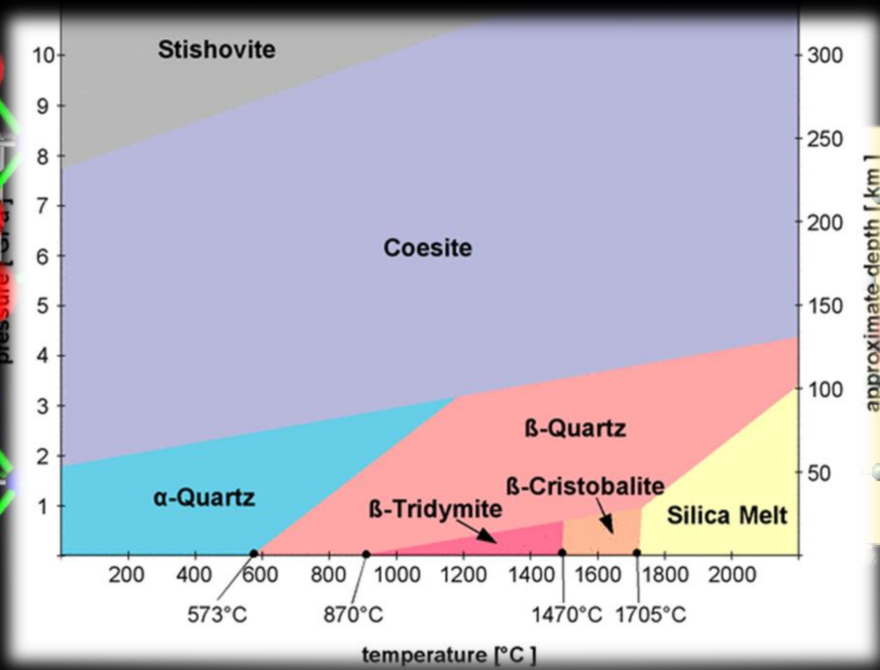
- Quartz

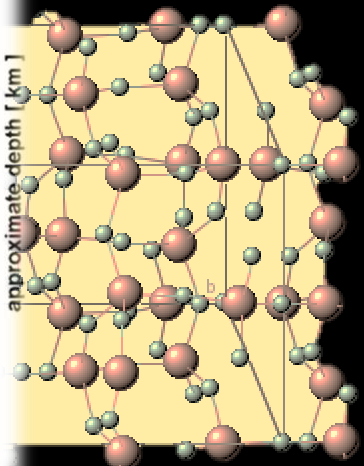
trigonal

- Coesite

monoclinic



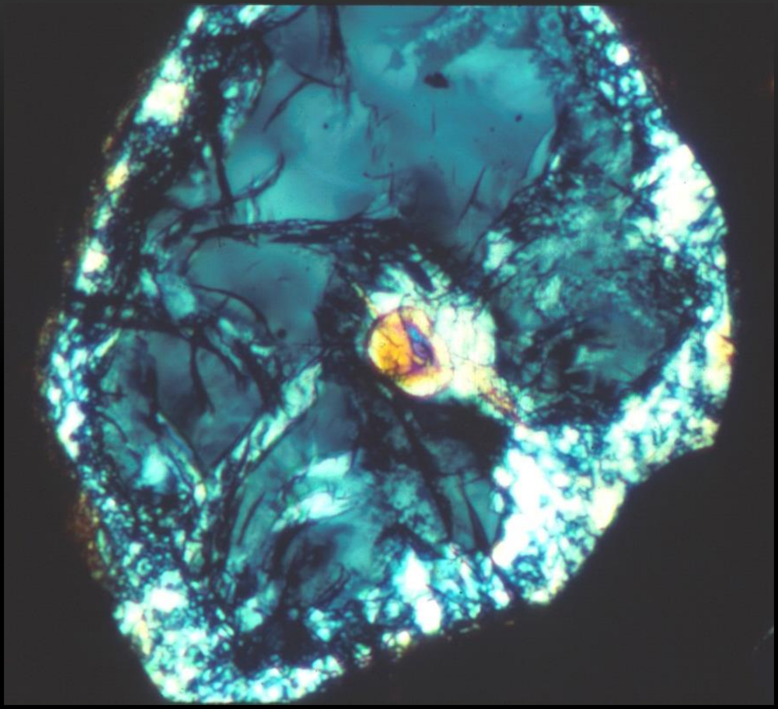


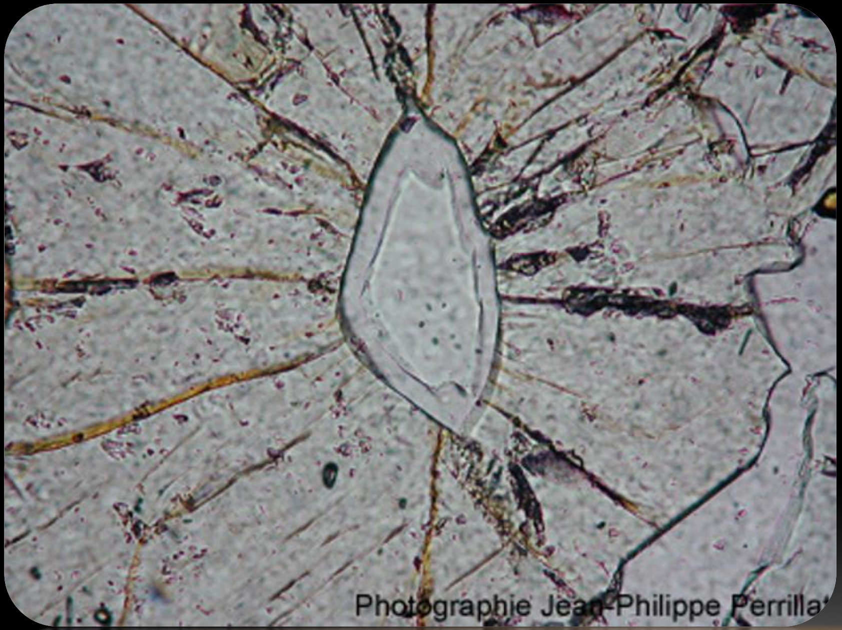


SiO$_2$ coesite

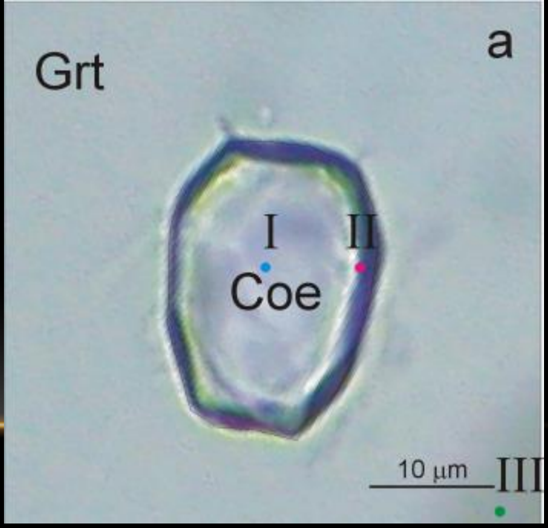
First found and described in

- **The Caledonides** by David Smith 1984, Nature, 310, 641-644 and
- **The Western Alps** by Christian Chopin 1984, CMP, 86, 107-118

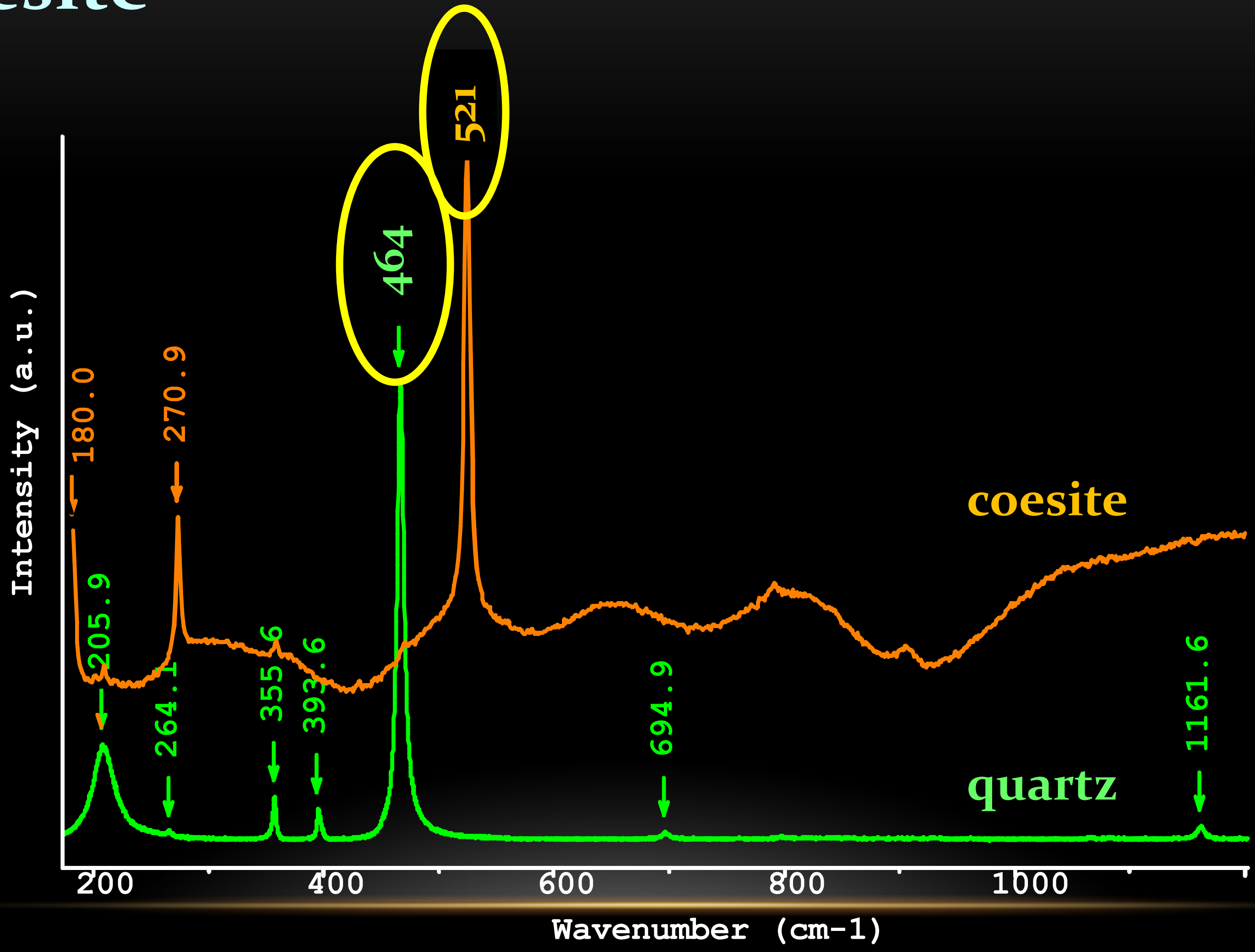




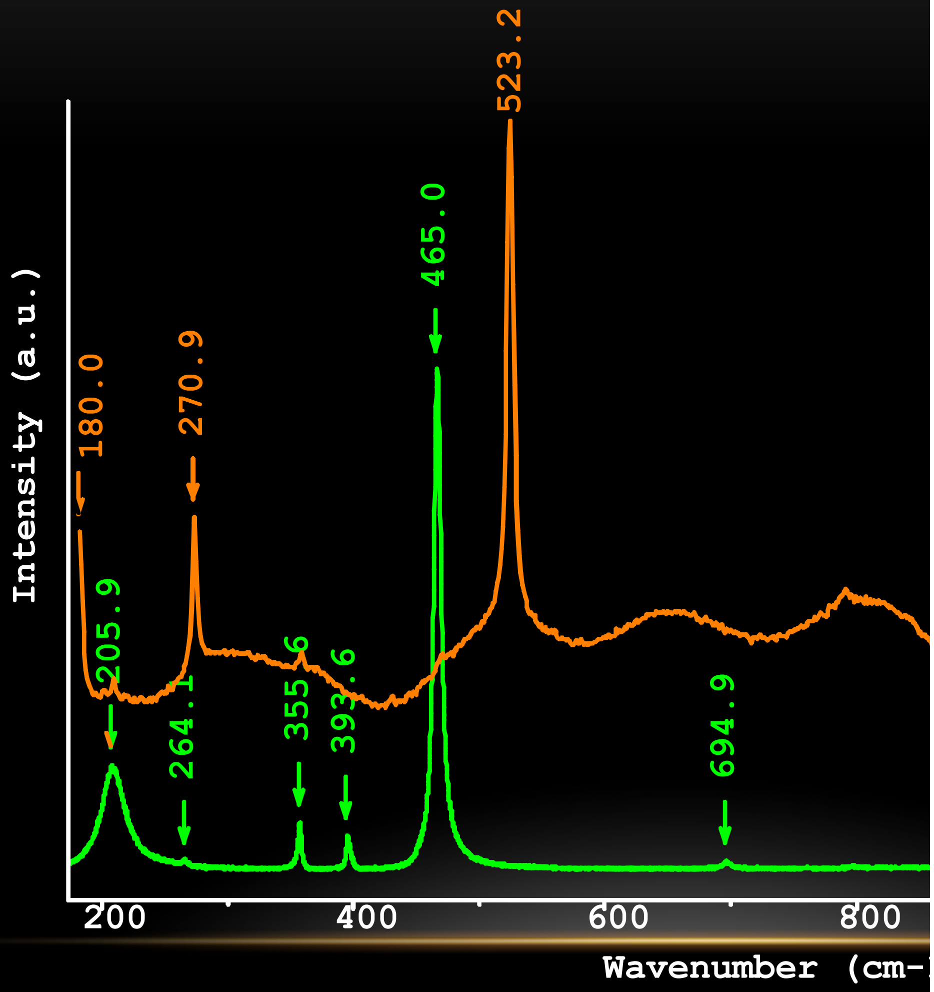
Photographie Jean-Philippe Perrillat

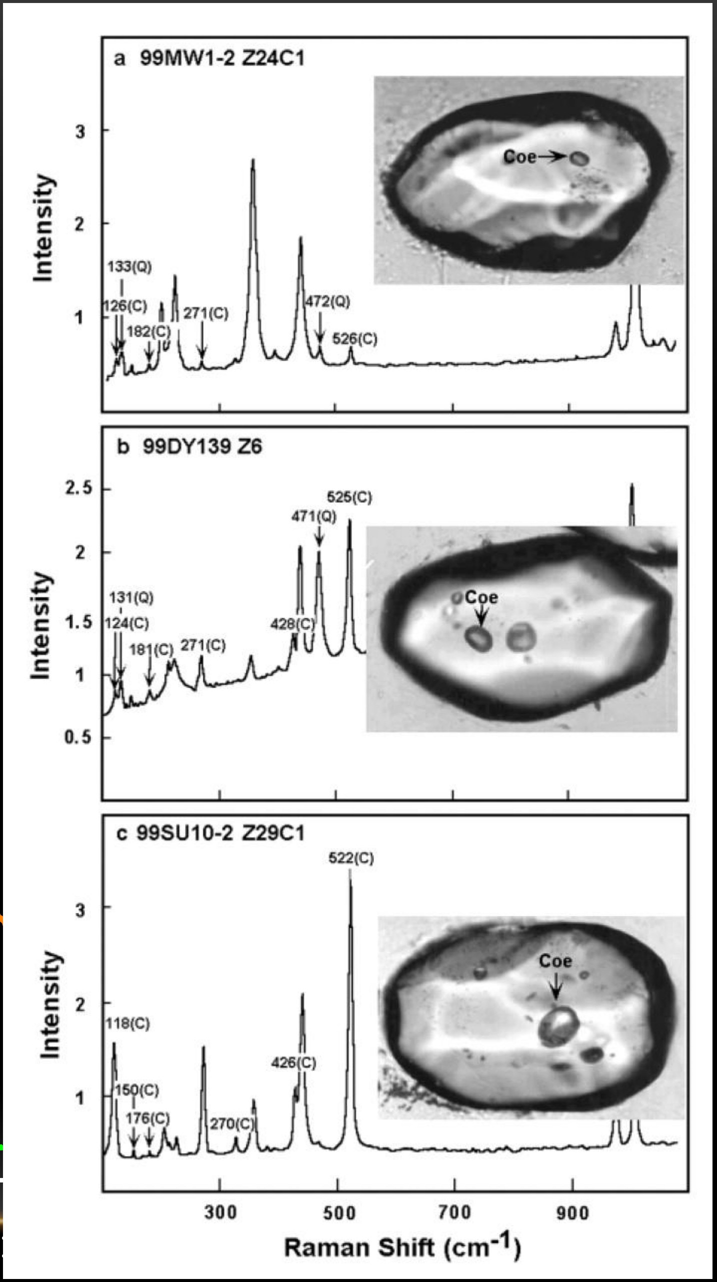


SiO_2 coesite



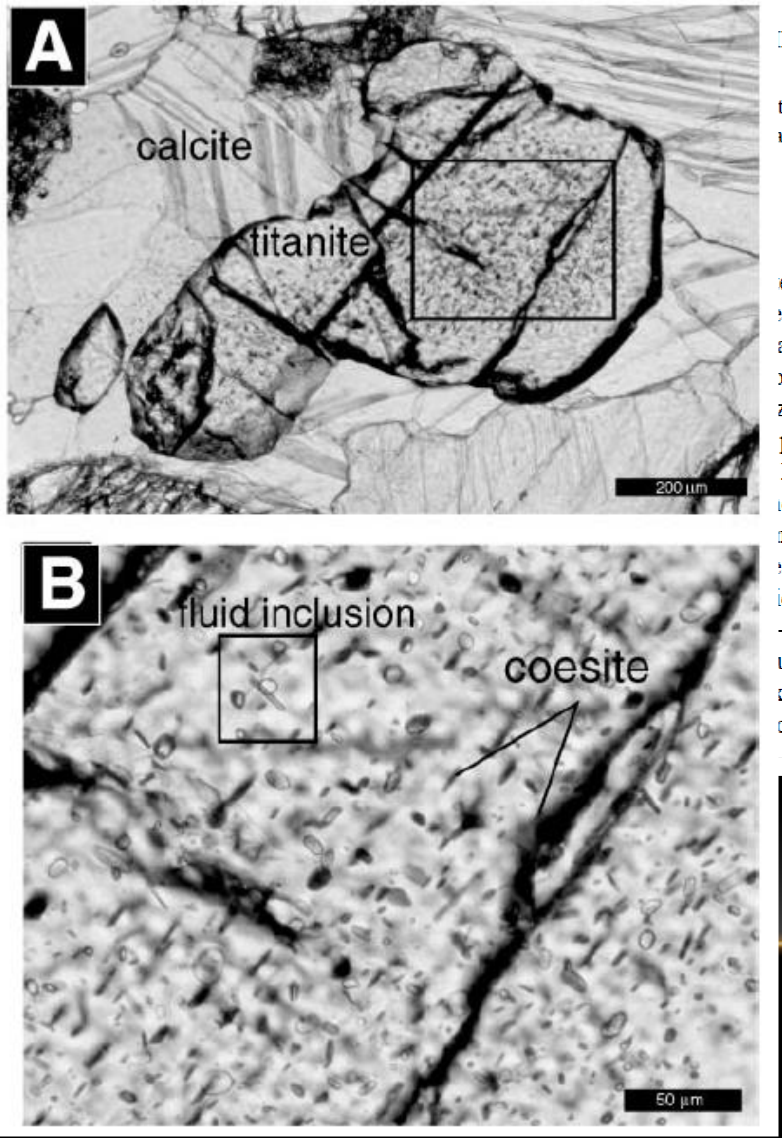
SiO_2 coesite

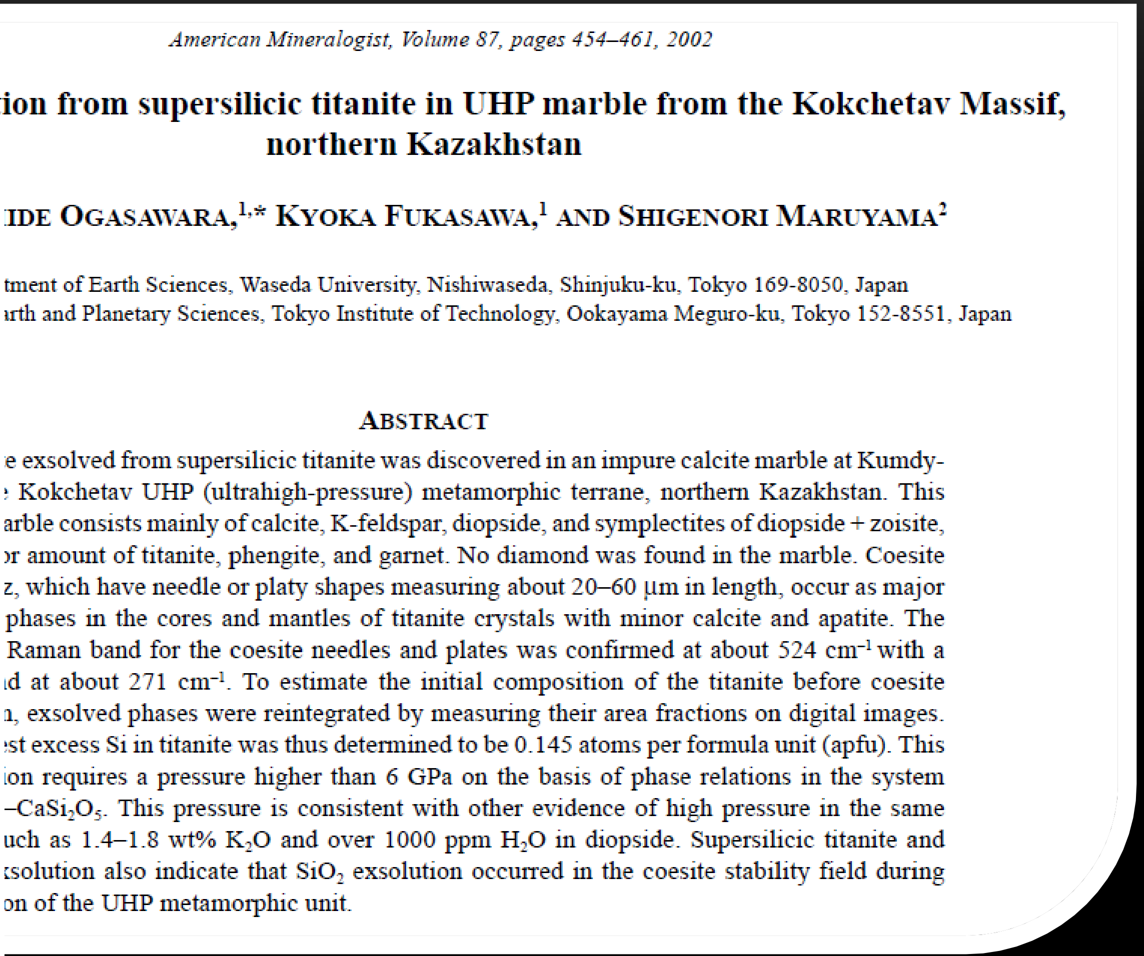




Coesite in zircons from DabieShan gneisses, Ye et al 2001 Am. Mineralogist, 86, 1151-1155

SiO2 coesite




American Mineralogist, Volume 87, pages 454–461, 2002

Coesite exsolution from supersilicic titanite in UHP marble from the Kokchetav Massif, northern Kazakhstan

IDE OGASAWARA,[1,*] KYOKA FUKASAWA,[1] AND SHIGENORI MARUYAMA[2]

tment of Earth Sciences, Waseda University, Nishiwaseda, Shinjuku-ku, Tokyo 169-8050, Japan
rth and Planetary Sciences, Tokyo Institute of Technology, Ookayama Meguro-ku, Tokyo 152-8551, Japan

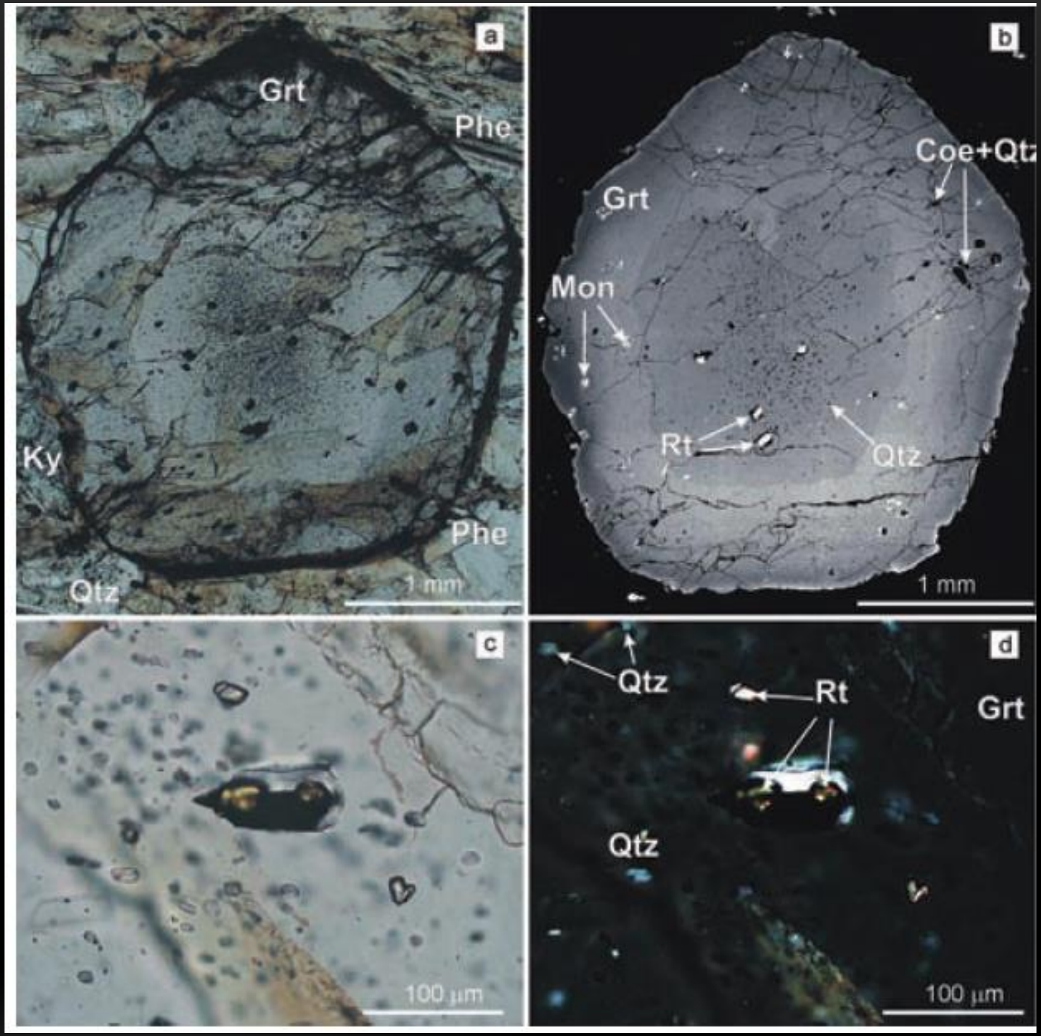
ABSTRACT

e exsolved from supersilicic titanite was discovered in an impure calcite marble at Kumdy-
Kokchetav UHP (ultrahigh-pressure) metamorphic terrane, northern Kazakhstan. This
arble consists mainly of calcite, K-feldspar, diopside, and symplectites of diopside + zoisite,
r amount of titanite, phengite, and garnet. No diamond was found in the marble. Coesite
z, which have needle or platy shapes measuring about 20–60 µm in length, occur as major
phases in the cores and mantles of titanite crystals with minor calcite and apatite. The
Raman band for the coesite needles and plates was confirmed at about 524 cm^{-1} with a
d at about 271 cm^{-1}. To estimate the initial composition of the titanite before coesite
n, exsolved phases were reintegrated by measuring their area fractions on digital images.
st excess Si in titanite was thus determined to be 0.145 atoms per formula unit (apfu). This
ion requires a pressure higher than 6 GPa on the basis of phase relations in the system
–$CaSi_2O_5$. This pressure is consistent with other evidence of high pressure in the same
uch as 1.4–1.8 wt% K_2O and over 1000 ppm H_2O in diopside. Supersilicic titanite and
solution also indicate that SiO_2 exsolution occurred in the coesite stability field during
on of the UHP metamorphic unit.

- **coesite exsolution in titanite → supersilisic titanite**
- **SiO2 exsolution occurred in the coesite stability field during exhumation of the UHP metamorphic unit**

SiO_2 quartz

Rock type:
Garnet mica schist
Location:
Barchi-Kole, Kokchetav Massif, Kazakhstan
Mineral assemblage:
Grt, Phe, Ky, Qtz/Coe(?), Gr, Ilm, Rut, Chl
Peak PT conditions:
600–650 °C 1.6–2.4 GPa



KORSAKOV A.V., PERRAKI M., ZHUKOV V.P., DE GUSSEM K., VANDENABEELE P., TOMILENKO A.A. 2009:.
European Journal of Mineralogy, 21, 1313-1324.

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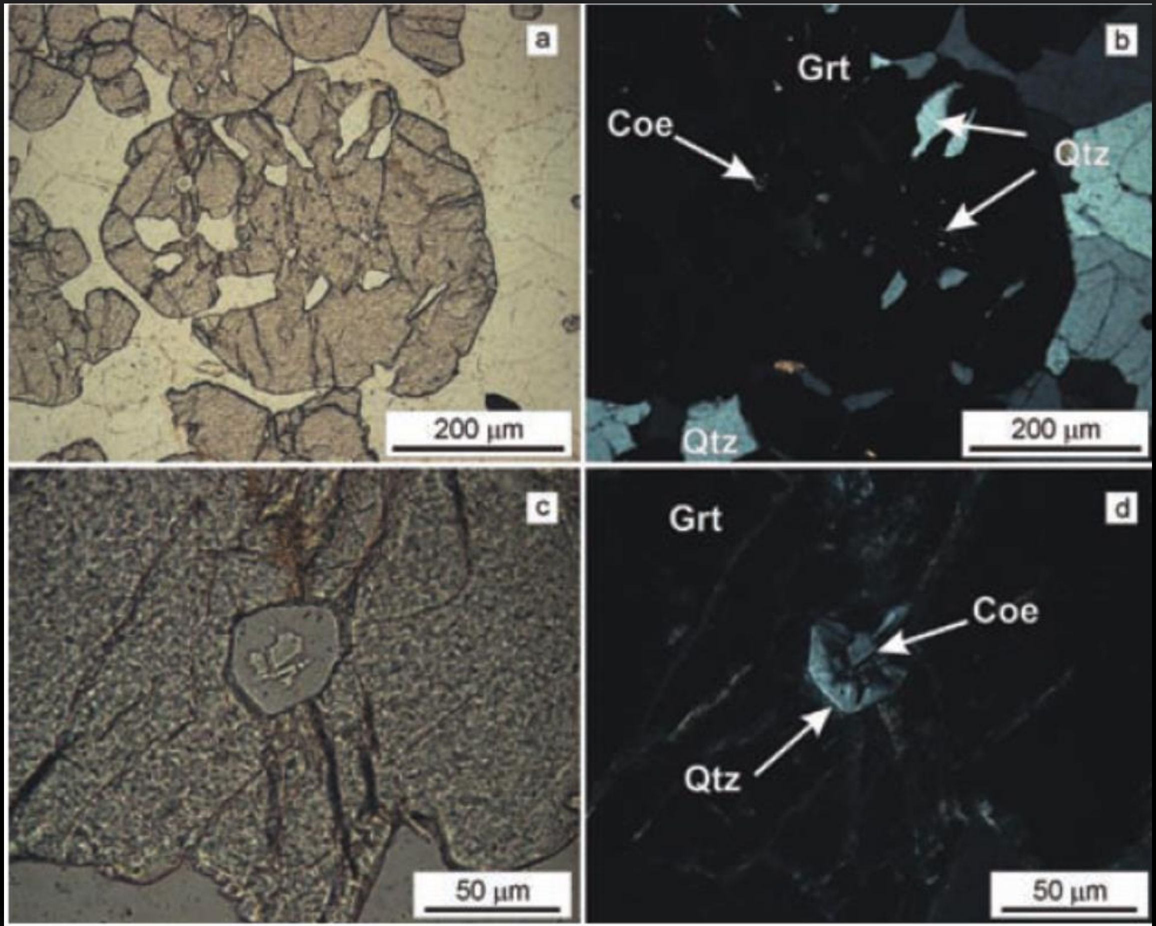

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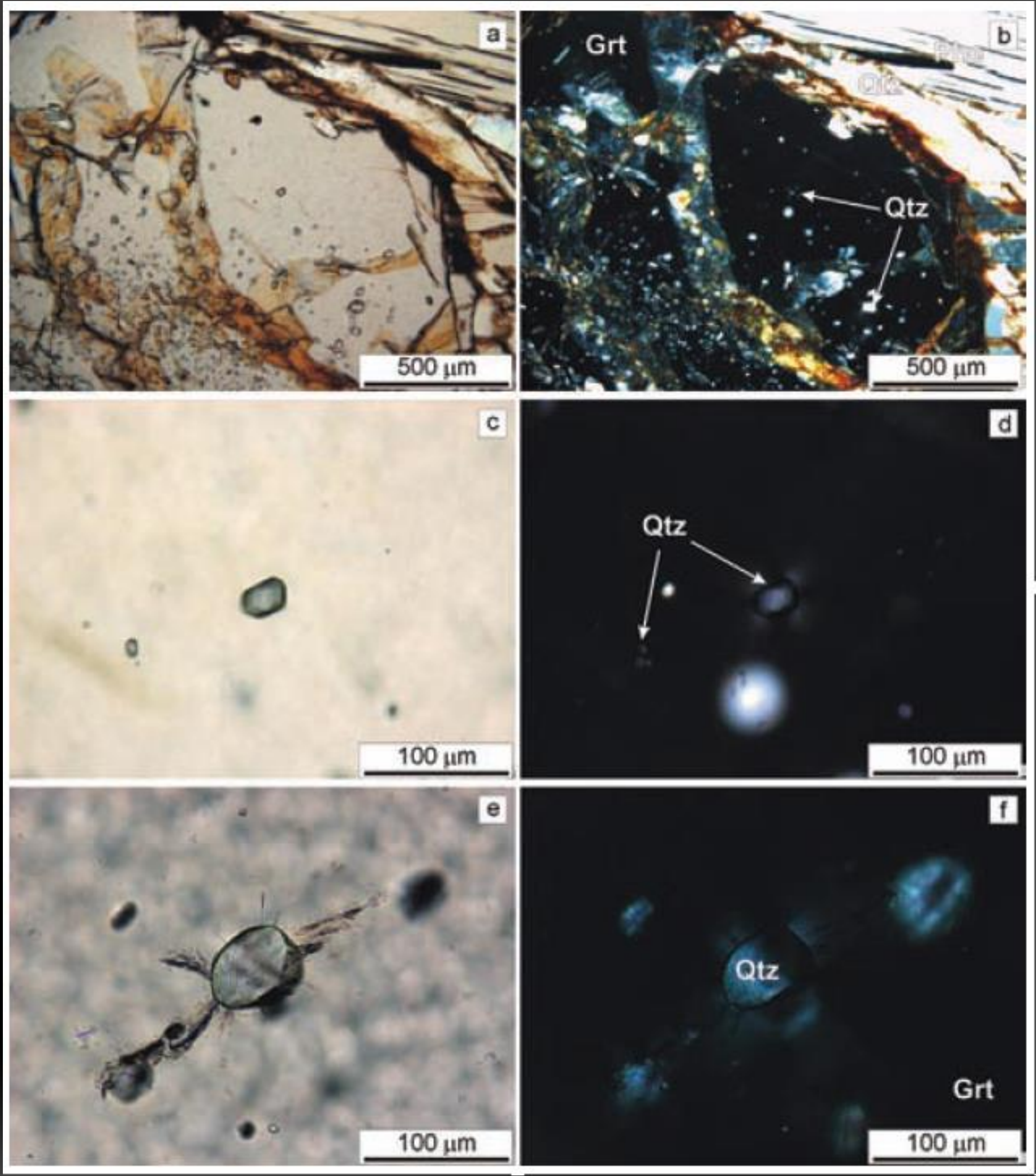

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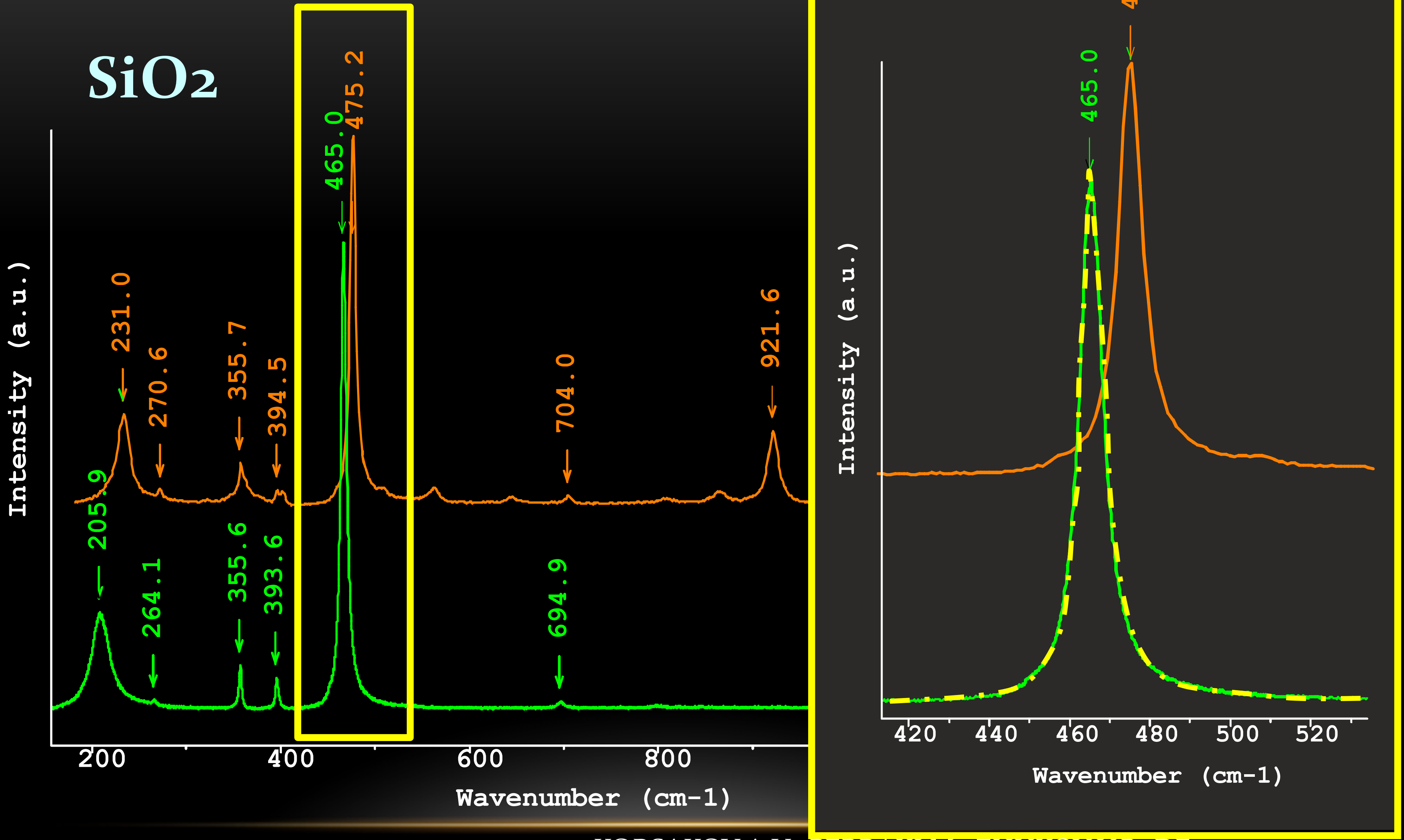
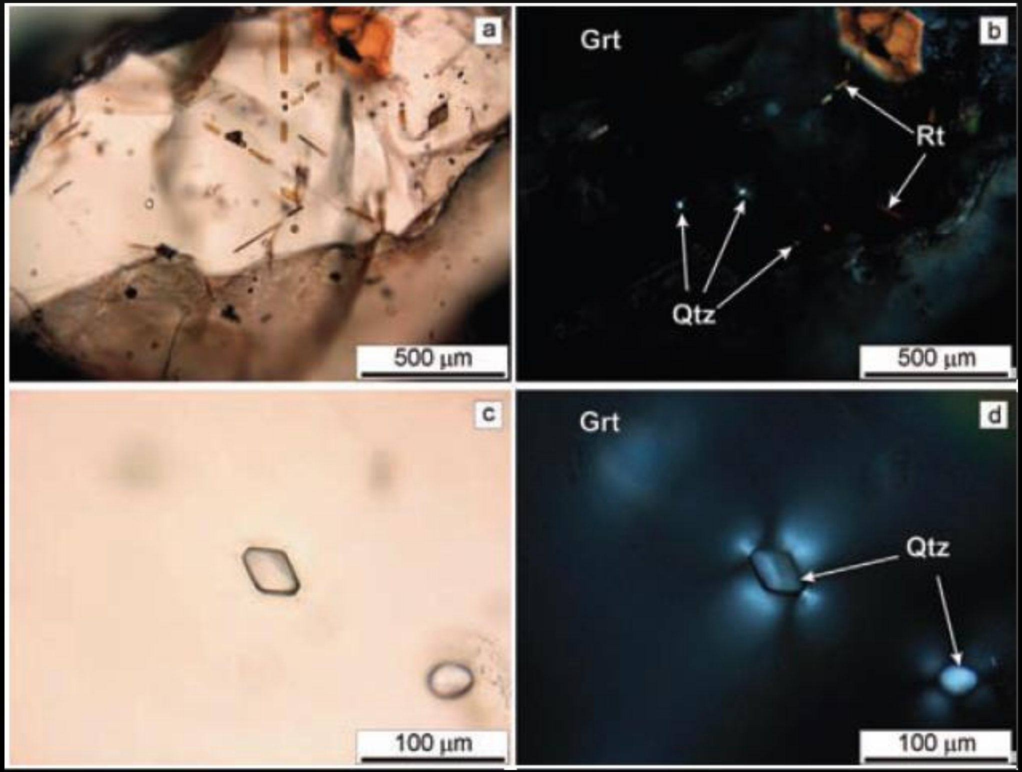
European Journal of Mineralogy, 21, 1313-1324.

SiO2



KORSAKOV A.V., PERRAKI M., ZHUKOV V.P., DE GUSSEM K., VANDENABEELE P., TOMILENKO A.A. **2009:.**
European Journal of Mineralogy, 21, 1313-1324.

SiO2
quartz



Roct type:

diamond-bearing eclogite xenolith

Location:

Mir kimberlite pipe (Yakutiya)

Mineral assemblage:

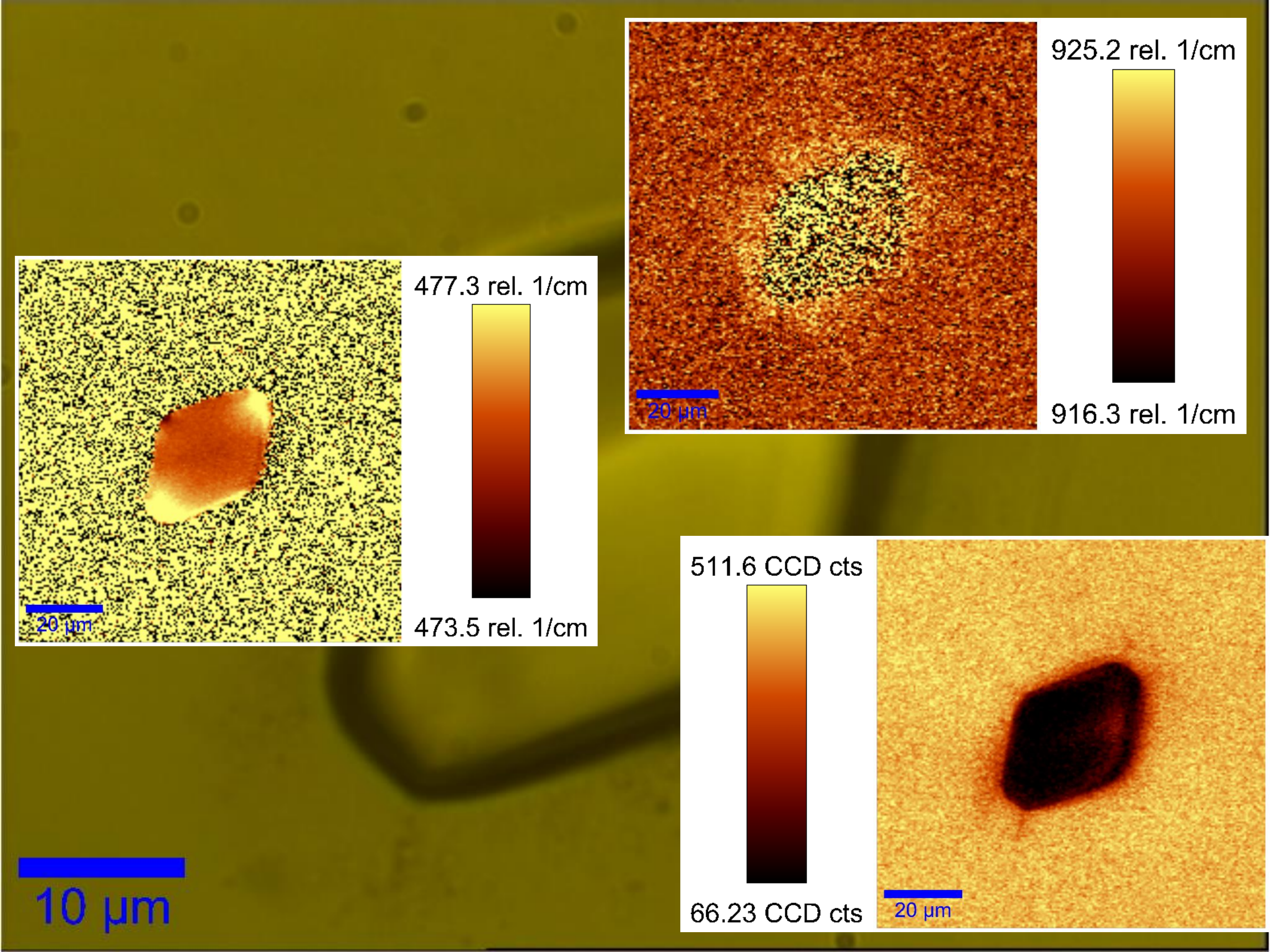
Grt, Cpx, Dia, Qtz, Ru

Peak PT conditions:

1100–1200 °C 5GPa

from Mir kimberlite pipe (Yakutiya, Russia)

KORSAKOV A.V., PERRAKI M., ZHUKOV V.P., DE GUSSEM K., VANDENABEELE P., TOMILENKO A.A. 2009:.
European Journal of Mineralogy, 21, 1313-1324.


925.2 rel. 1/cm
916.3 rel. 1/cm
20 µm
477.3 rel. 1/cm
473.5 rel. 1/cm
20 µm
511.6 CCD cts
66.23 CCD cts
20 µm
10 µm

American Mineralogist, Volume 92, pages 1303–1315, 2007

Laser Raman microspectrometry of metamorphic quartz: A simple method for comparison of metamorphic pressures

MASAKI ENAMI,[1,*] TADAO NISHIYAMA,[2] AND TAKASHI MOURI[1]

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[2]Department of Earth and Environment, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

ABSTRACT

A Laser Raman microspectrometry method was applied to metamorphic quartz in quartz-eclogite-, epidote-amphibolite-, and amphibolite-facies rocks to assess the quantitative correlation between the Raman frequency shift and metamorphic pressure. Quartz crystals sealed in garnet and other phases have a higher frequency shift than those in the matrix
frequency shift specific to the individual host crystals
epidote). These observations imply that the residual pr
on elastic parameters of the host crystals, as discussed b
shift of quartz inclusions in garnet systematically incre
sures from the amphibolite facies (0.30–0.55 GPa/470–5
(0.8–1.1 GPa/470–635 °C) to the quartz-eclogite facies (
on experimental work suggest that the measured Rama
of 0.1–0.2, 0.4–0.6, and 0.8–1.0 GPa for these three gro
mal stresses (internal pressures) of quartz inclusions in
model, and inferred pressure-temperature conditions at
the residual pressures estimated from the frequency shi
of quartz is a simple and effective method for (1) comp
rocks formed under various pressure-temperature cond
signature in metamorphic rocks extensively recrystall
hydration stage.

Keywords: Raman shift, quartz, residual pressure,

s: α-quartz,

and stishovite is
pressure
nd-anvil cell that
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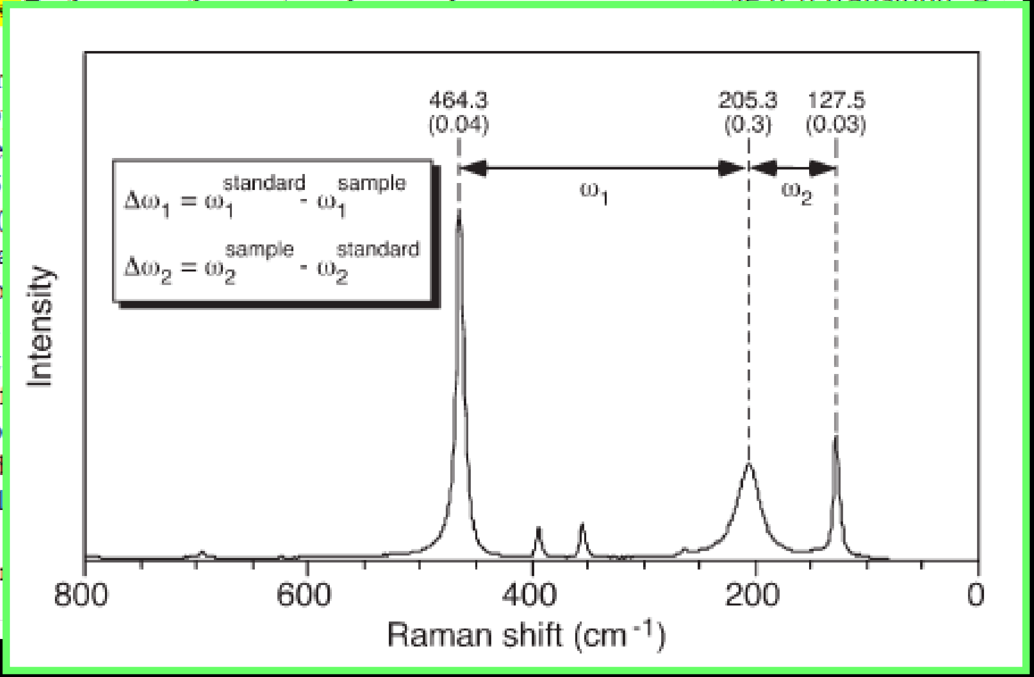


Numerical modeling of coesite-to-quartz transformation considering a 3-shelled elastic sphere in linear elasticity

- The system consists of pyrope and coesite at T_o and P_o, with coesite being completely transformed to α-quartz
- At the final stage the garnet host is at ambient conditions

- The residual presence for quartz inclusions should be as high as 3 GPa

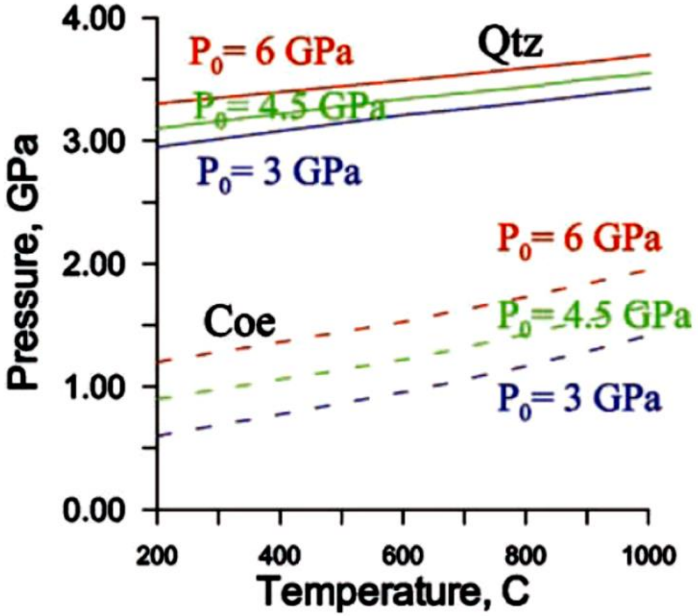
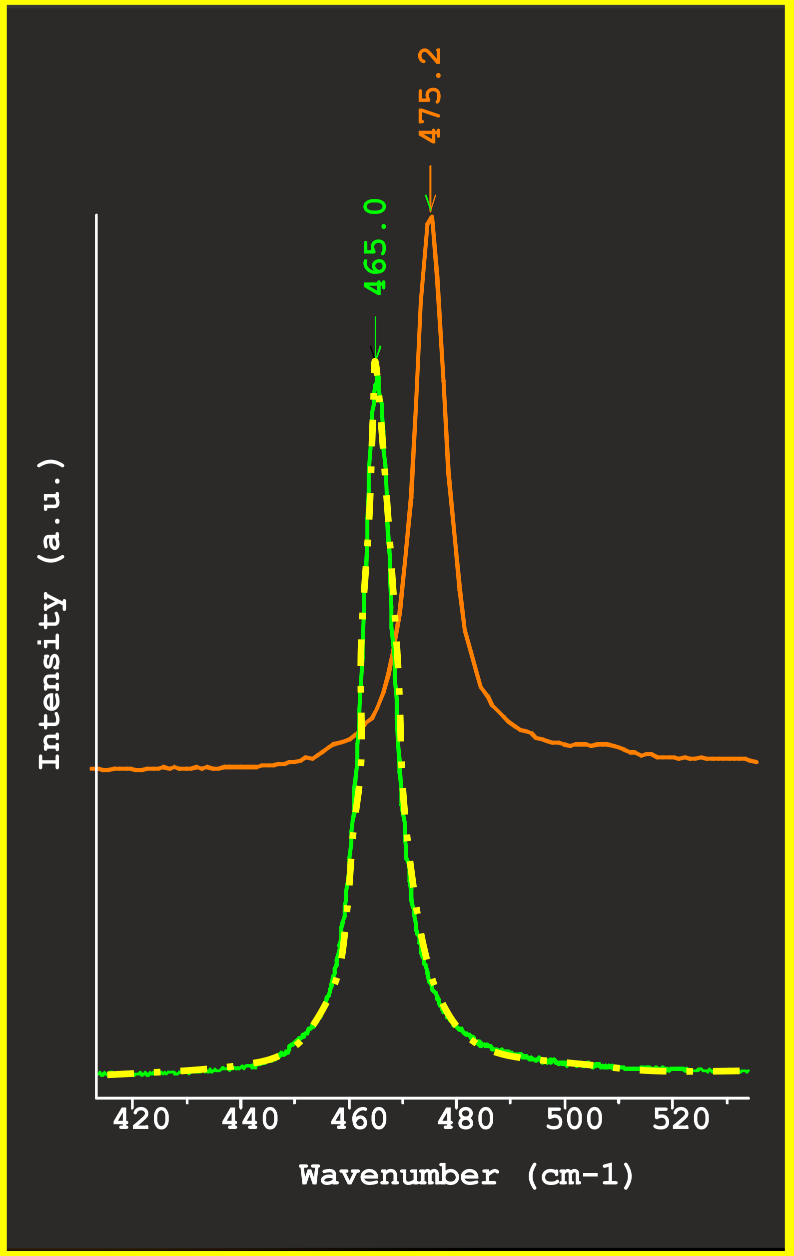


Fig. 8. Dependence of the residual pressure in coesite inclusions P_{in} on T_0 for different P_0 without phase transitions (dashed lines) and quartz inclusions (solid line) formed after complete transformation to quartz of original coesite inclusions.

KORSAKOV A.V., PERRAKI M., ZHUKOV V.P., DE GUSSEM K., VANDENABEELE P., TOMILENKO A.A. **2009:.**
European Journal of Mineralogy, 21, 1313-1324.

SiO2

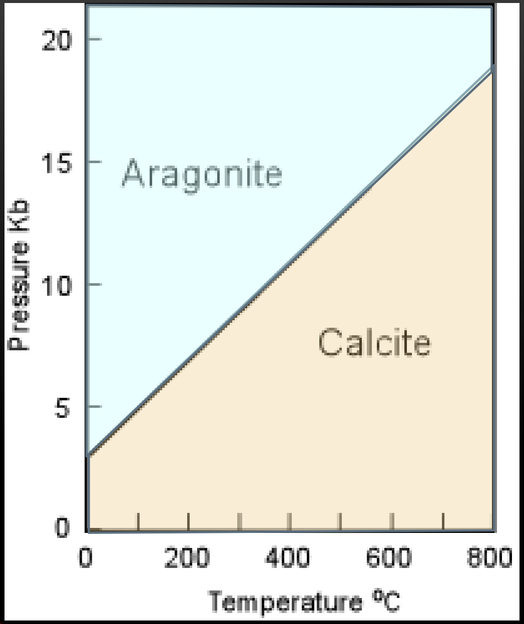
- Monocrystalline quartz inclusions with residual pressure up to 1.2 GPa (shift of the main quartz Raman band up to 474 cm^{-1}) might be considered as indirect evidence for UHPM conditions.
- Monocrystalline quartz inclusions with residual pressure above 2.5 GPa would clearly indicate that these quartz inclusions were coesite, which transformed to quartz.



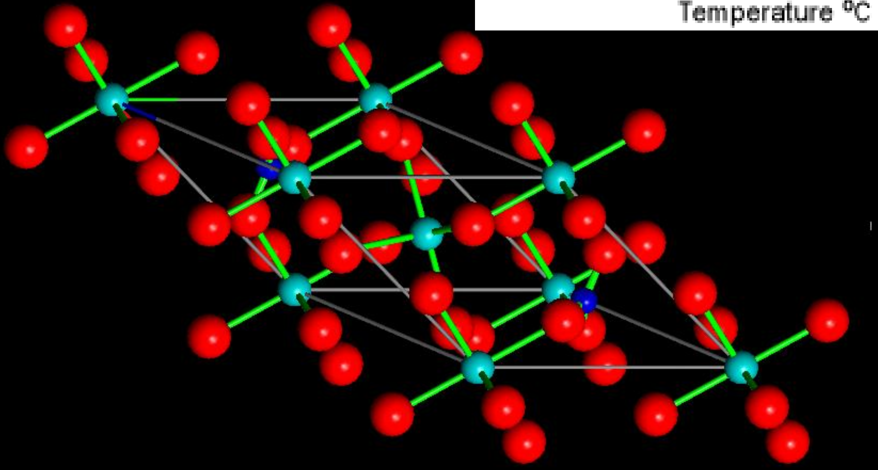
KORSAKOV A.V., PERRAKI M., ZHUKOV V.P., DE GUSSEM K., VANDENABEELE P., TOMILENKO A.A. 2009:.
European Journal of Mineralogy, 21, 1313-1324.

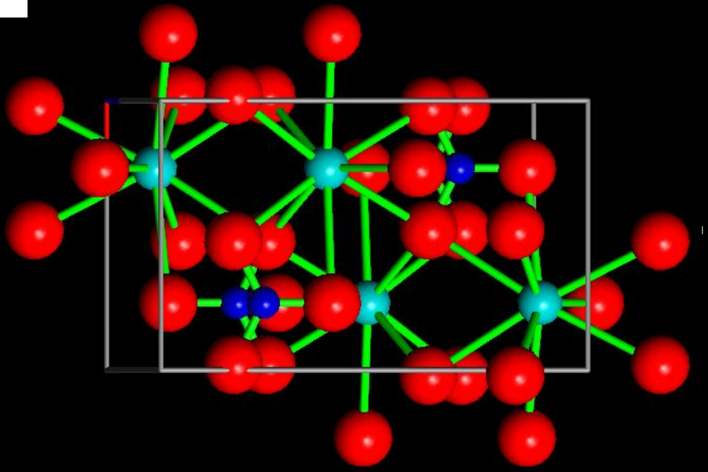
CaCO3

- Calcite
- Trigonal

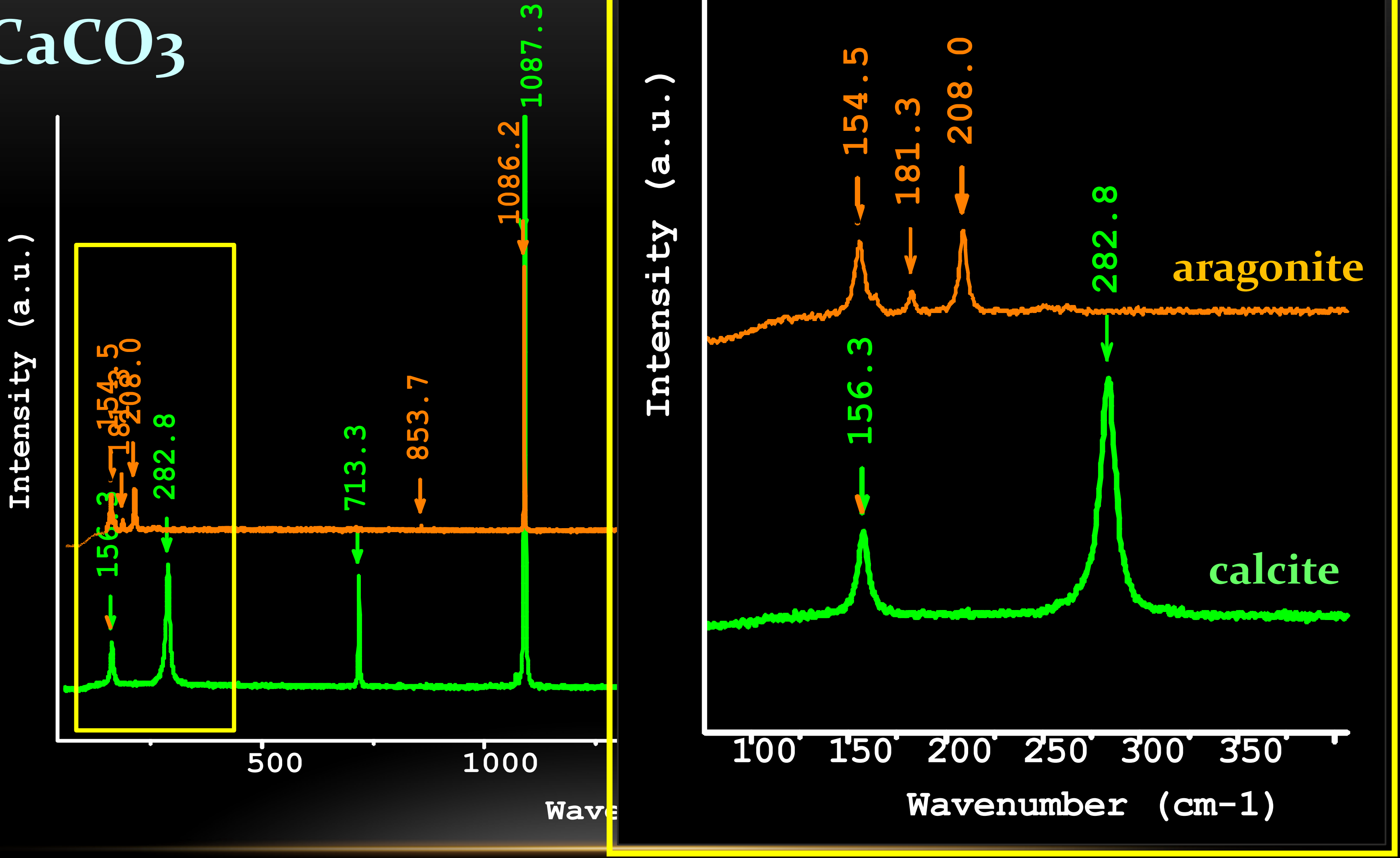


- Aragonite
- Orthorhombic



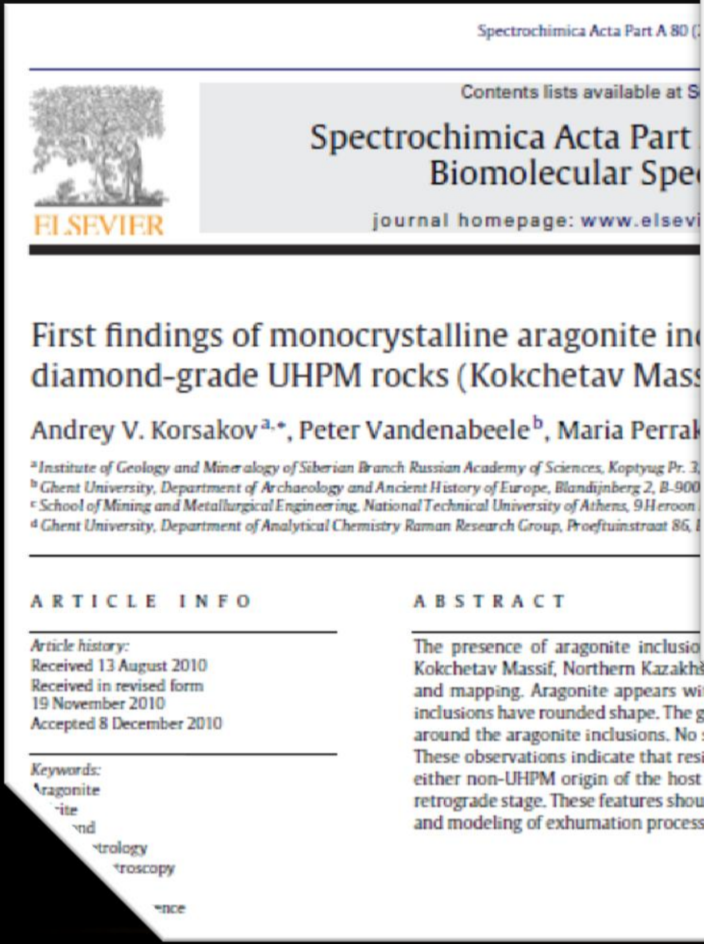


$CaCO_3$



Intensity (a.u.)
154.5
181.3
208.0
156.3
282.8
713.3
853.7
1086.2
1087.3
500
1000
Wave
Intensity (a.u.)
154.5
181.3
208.0
282.8
aragonite
156.3
calcite
100
150
200
250
300
350
Wavenumber (cm-1)

CaCO$_3$



Spectrochimica Acta Part A 80 (

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Biomolecular Spe

journal homepage: www.elsevi

First findings of monocrystalline aragonite in diamond-grade UHPM rocks (Kokchetav Mass

Andrey V. Korsakov[a,*], Peter Vandenabeele[b], Maria Perrak

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[b] Ghent University, Department of Archaeology and Ancient History of Europe, Blandijnberg 2, B-900
[c] School of Mining and Metallurgical Engineering, National Technical University of Athens, 9 Heroon
[d] Ghent University, Department of Analytical Chemistry Raman Research Group, Proeftuinstraat 86,

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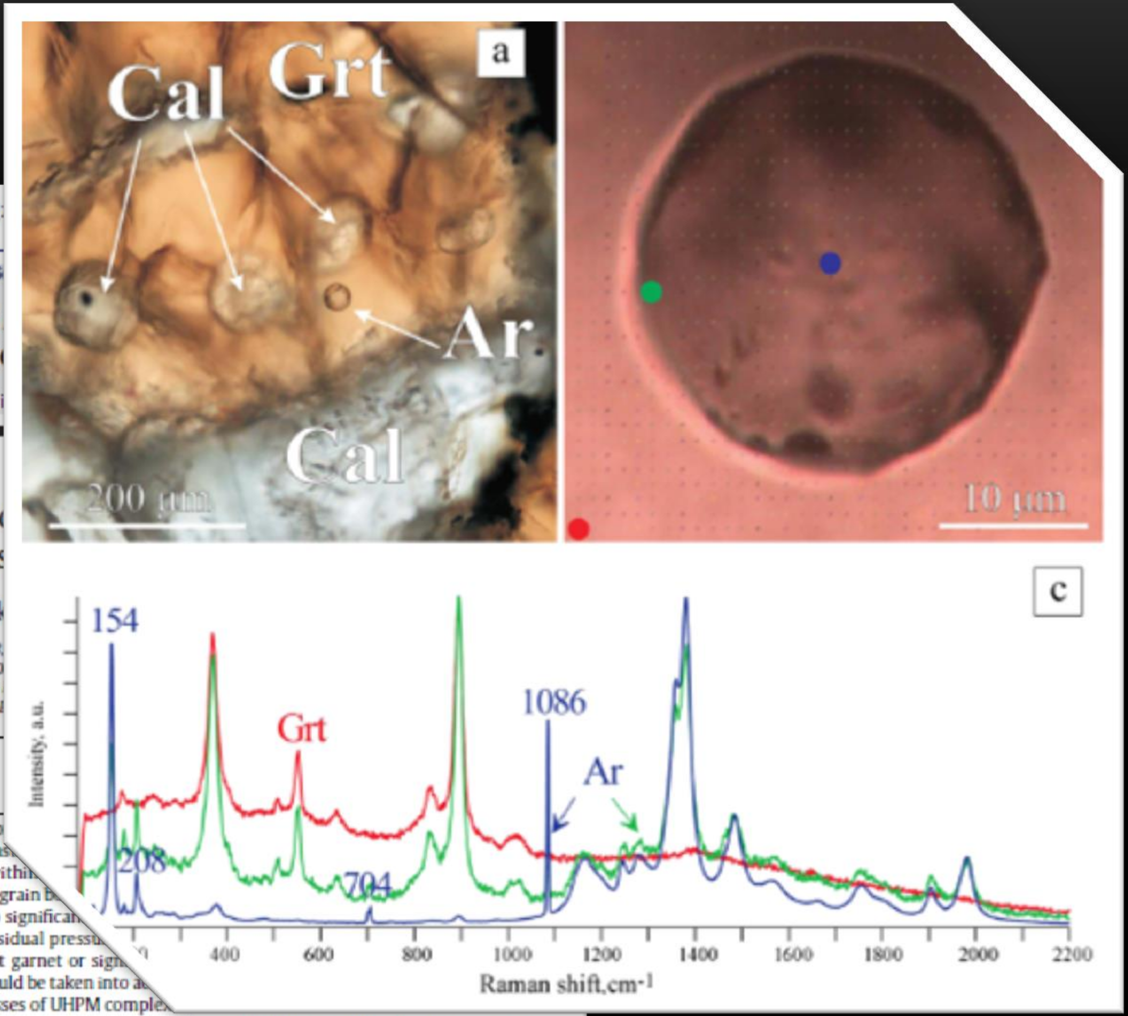
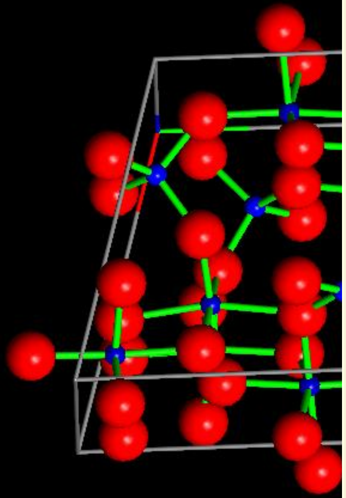
ABSTRACT

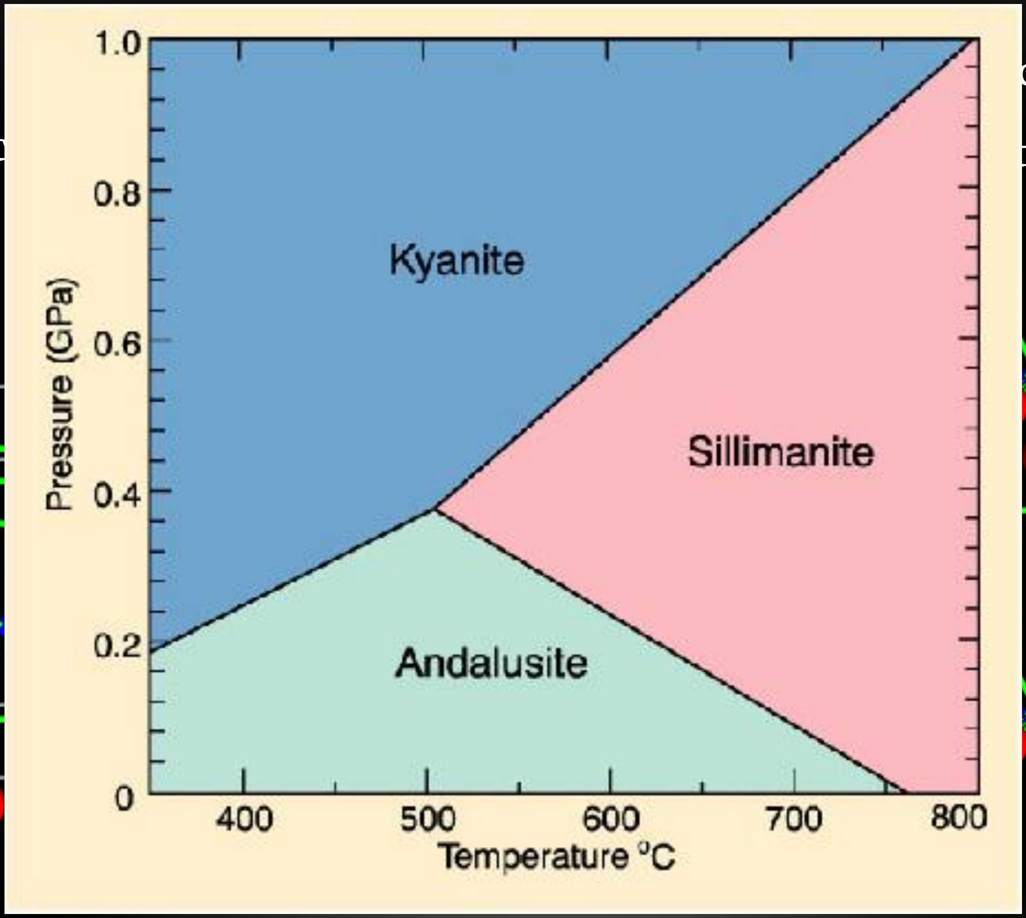
The presence of aragonite inclusio
Kokchetav Massif, Northern Kazakhs
and mapping. Aragonite appears withi
inclusions have rounded shape. The grain b
around the aragonite inclusions. No significa
These observations indicate that residual pressu
either non-UHPM origin of the host garnet or sign
retrograde stage. These features should be taken into a
and modeling of exhumation processes of UHPM comple

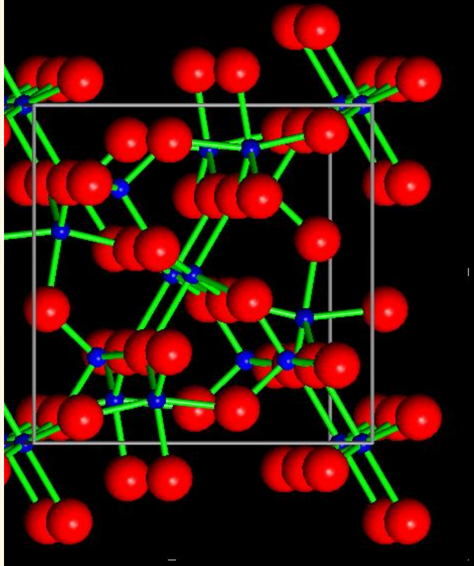


Al2SiO5

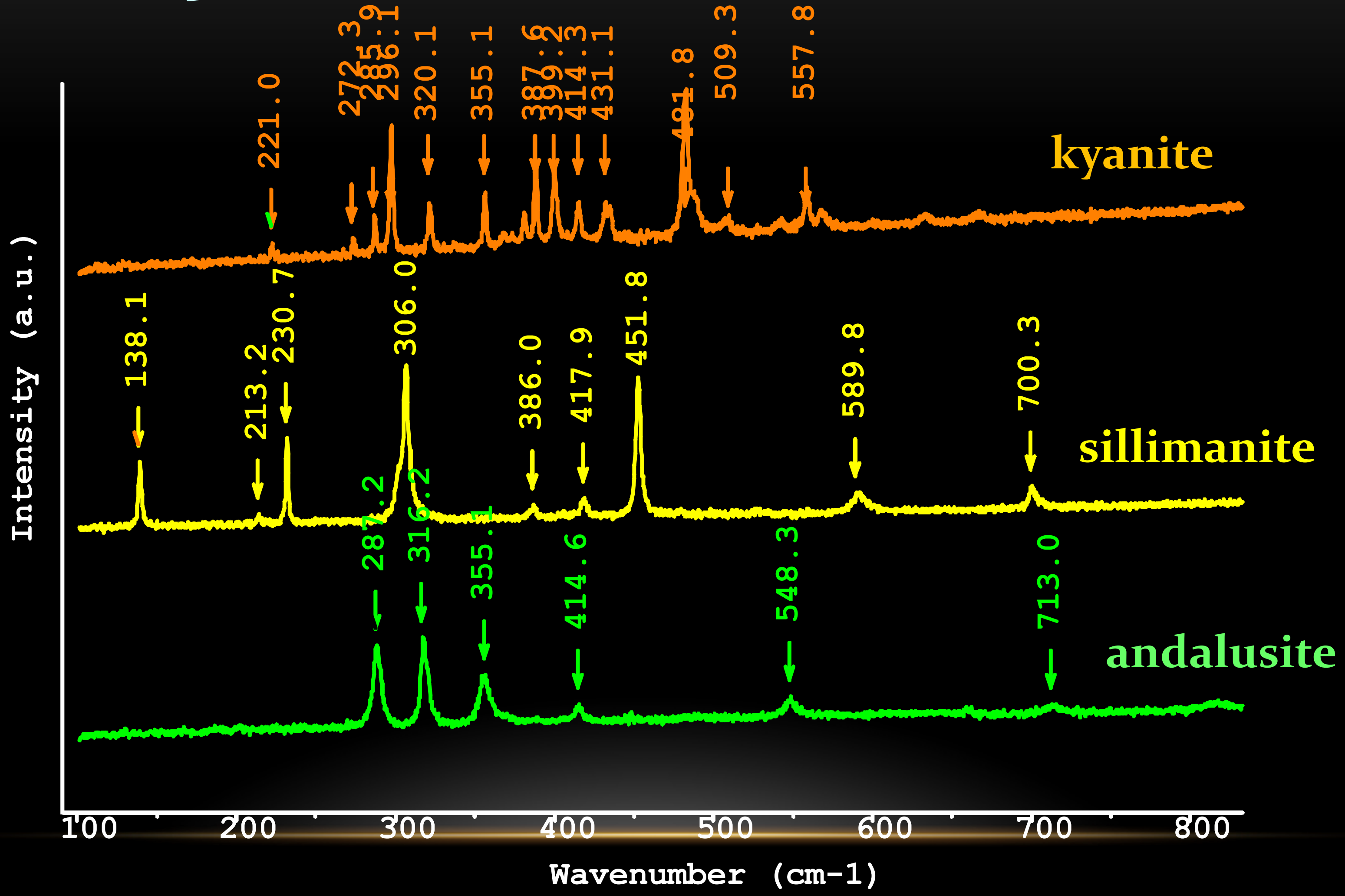
- Kyanite dalusite
- Triclinic thorhombic



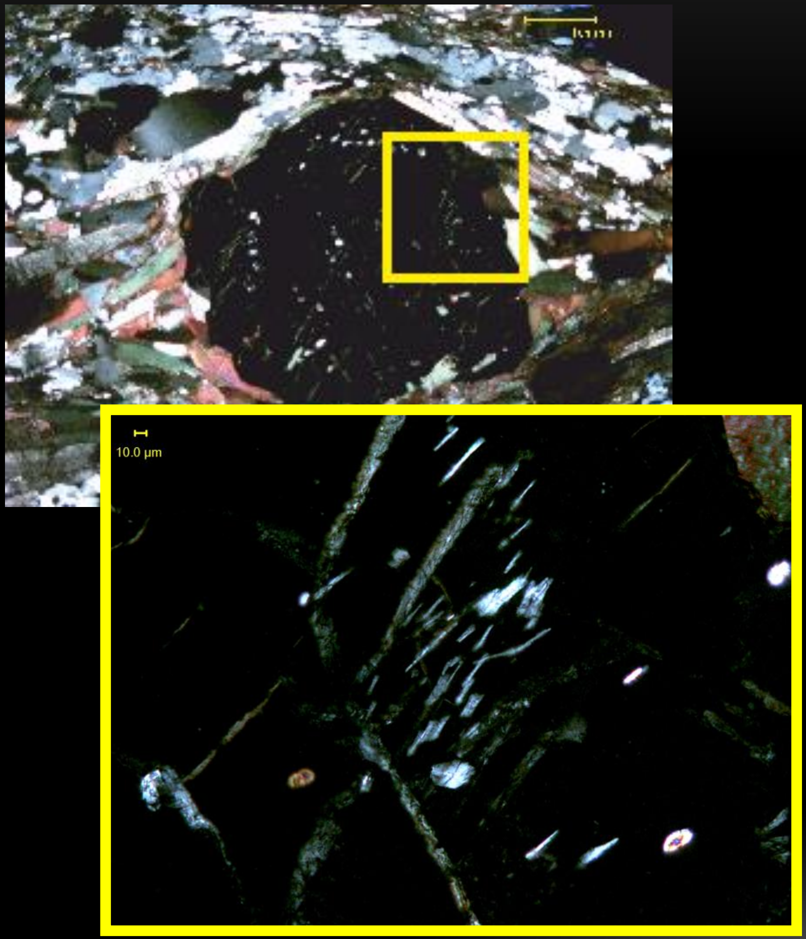


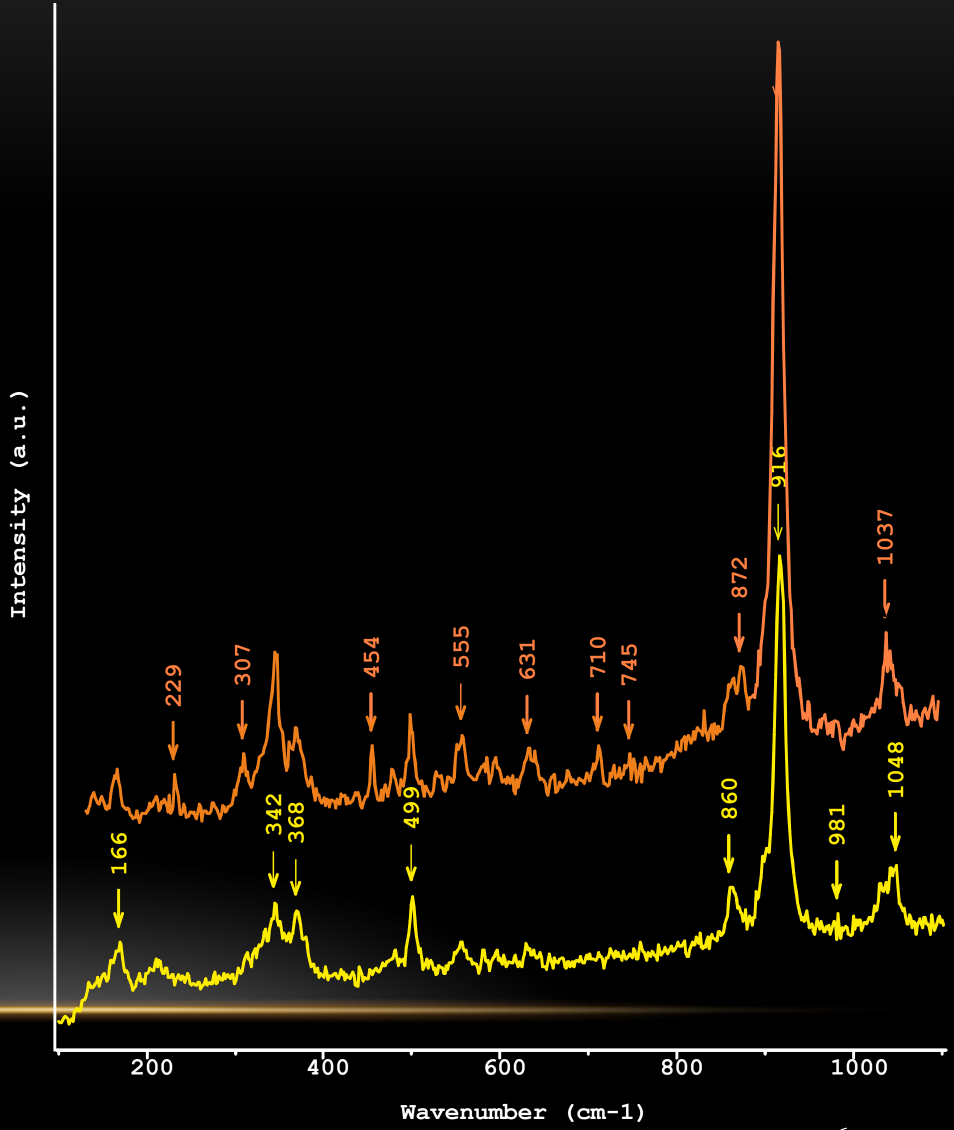


Al_2SiO_5


kyanite
221.0
272.3
285.9
296.1
320.1
355.1
387.6
399.2
414.3
431.1
481.8
509.3
557.8
sillimanite
138.1
213.2
230.7
306.0
386.0
417.9
451.8
589.8
700.3
andalusite
287.2
316.2
355.1
414.6
548.3
713.0
Intensity (a.u.)
100
200
300
400
500
600
700
800
Wavenumber (cm-1)

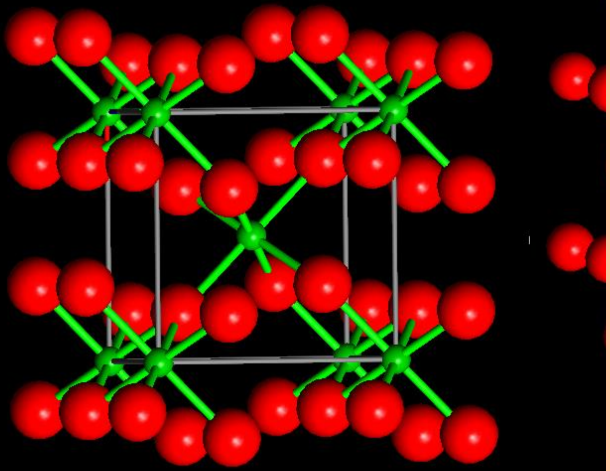
Al2SiO5 inclusions in diamond bearing garnet, Rhodope

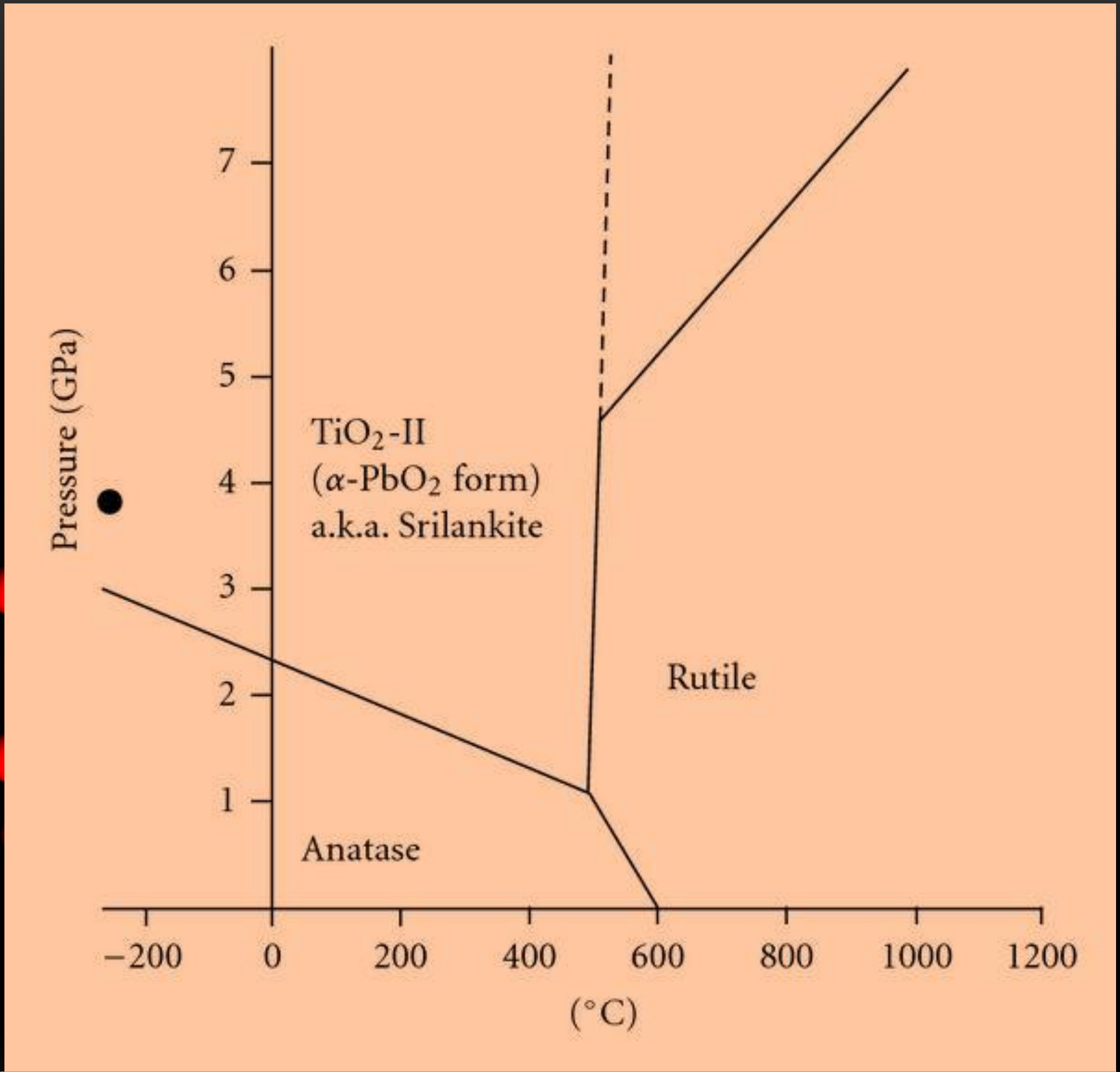




TiO2

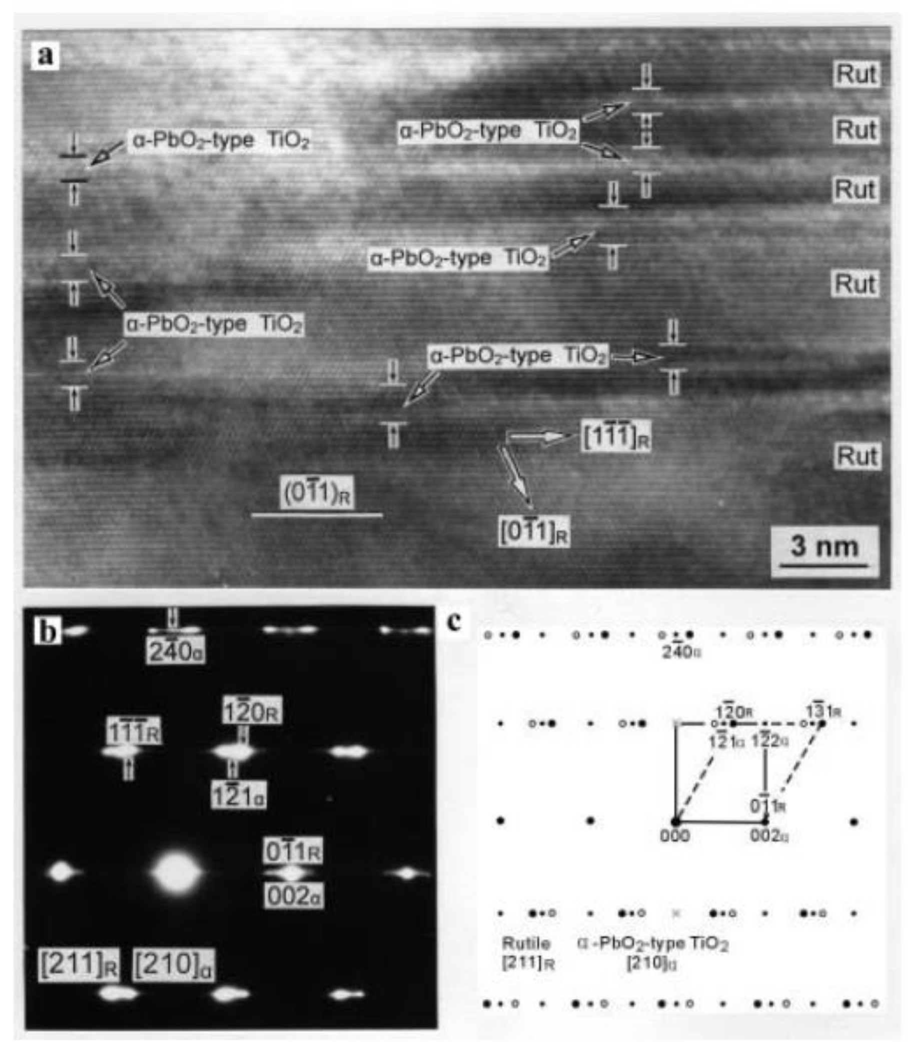
Rutile

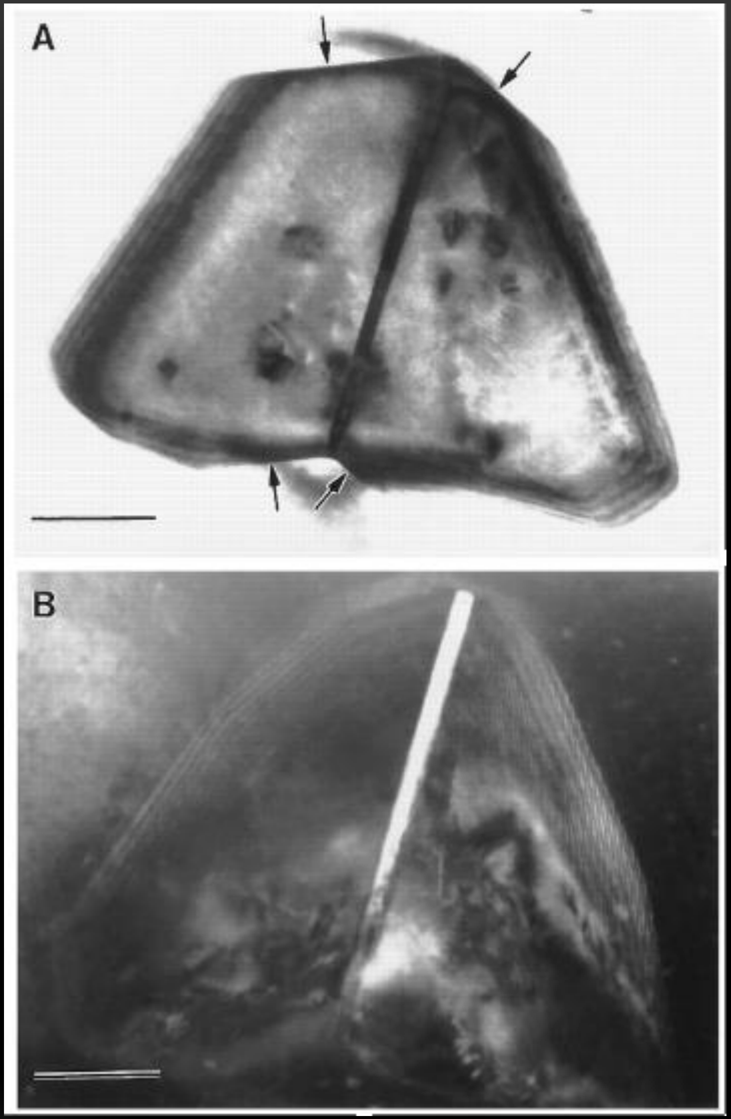




R. Ren, Z. Yang, and L. L. Shaw, "Polymorphic transformation and powder characteristics of TiO2 during high energy milling," Journal of Materials Science, vol. 35, no. 23, pp. 6015–6026, 2000.
A. C. Withers, E. J. Essene, and Y. Zhang, "Rutile/TiO2II phase equilibria," *Contributions to Mineralogy and Petrology*, vol. 145, no. 2, pp. 199–204, 2003.

TiO_2 with α-PbO_2 structure

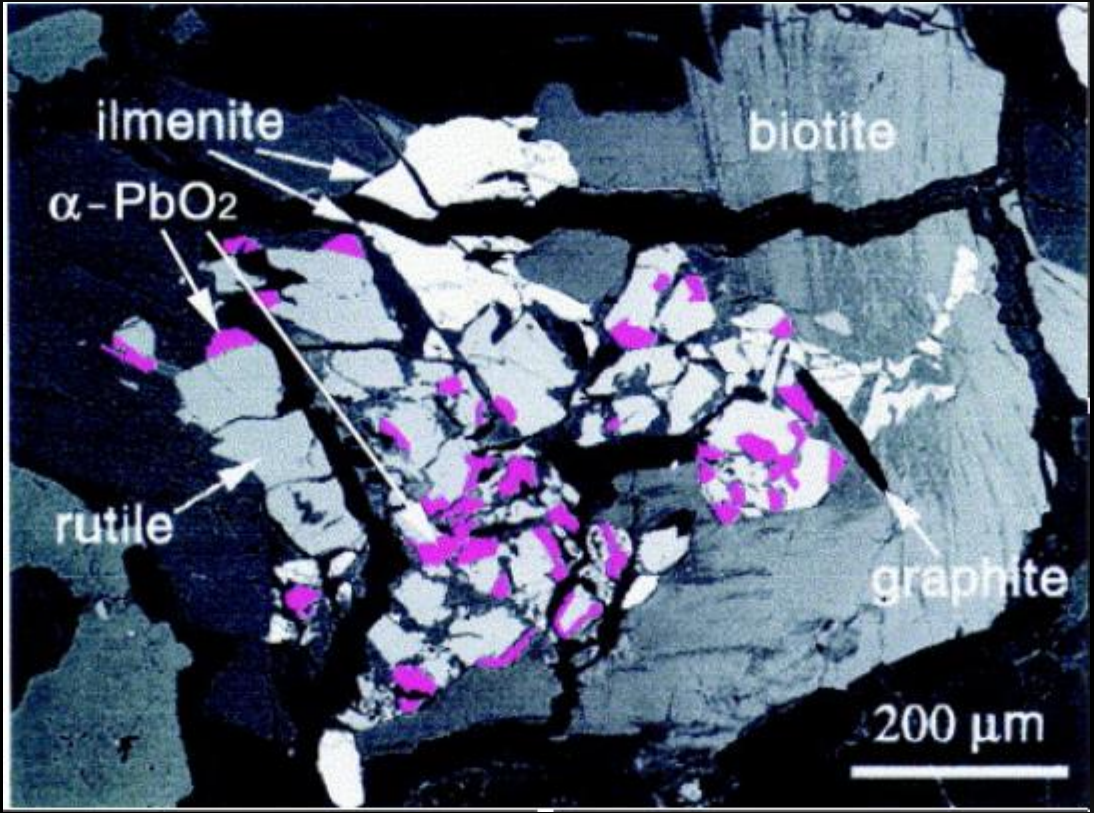


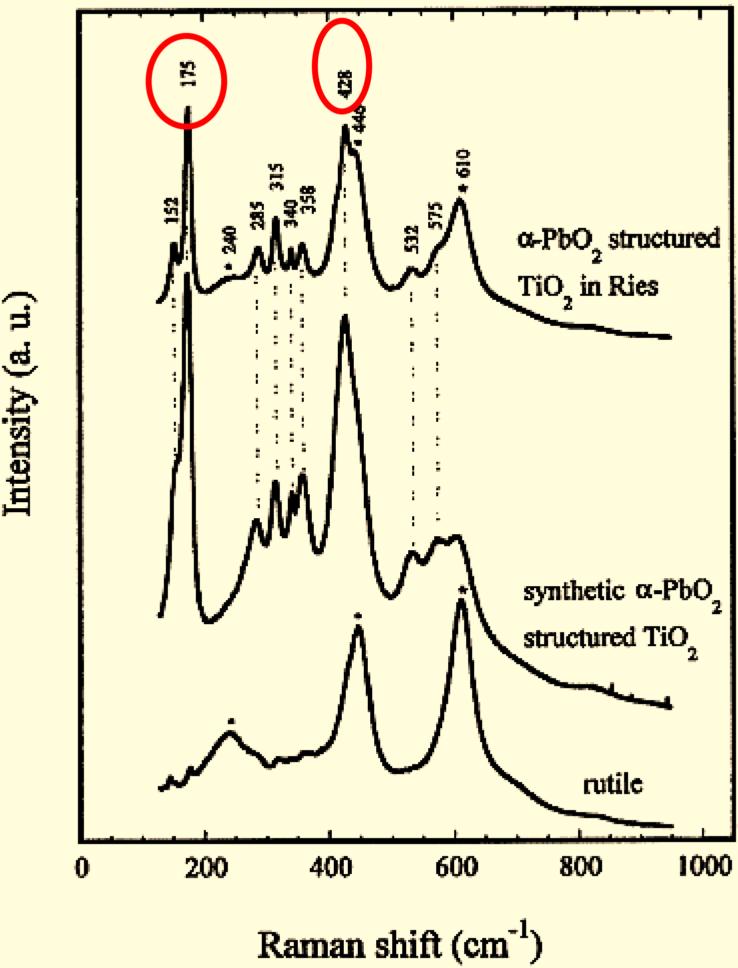


α-PbO_2-type nanophase , coesite-bearing eclogite, Dabie Mountains, China
Wu et al 2005 American Mineralogist 90 *1458-1461*

diamondiferous quartzofeldspathic rocks from the Saxonian Erzgebirge, Germany
Hwang et al 2000 Science, 288, 321

TiO_2 with α-PbO_2 structure



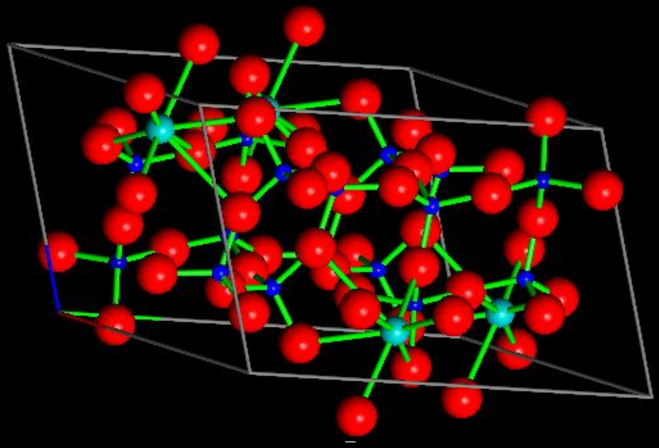


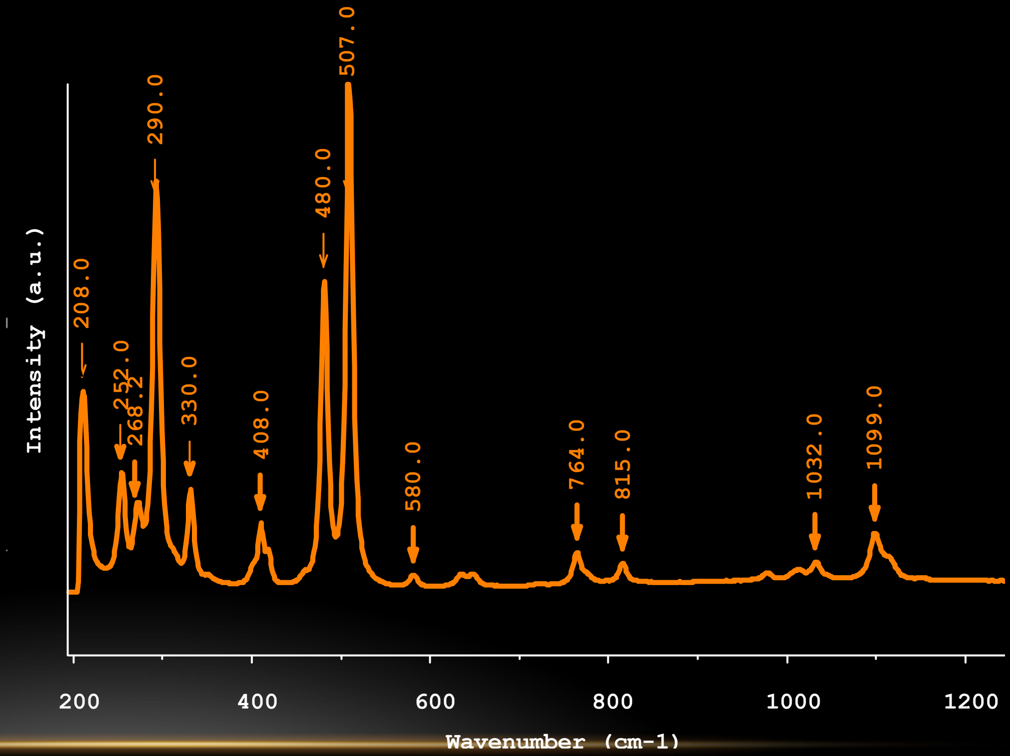
Shocked garnet gneisses, Ries Crater, Germany
El Goresy et al 2001, EPSL, 182, 485-495

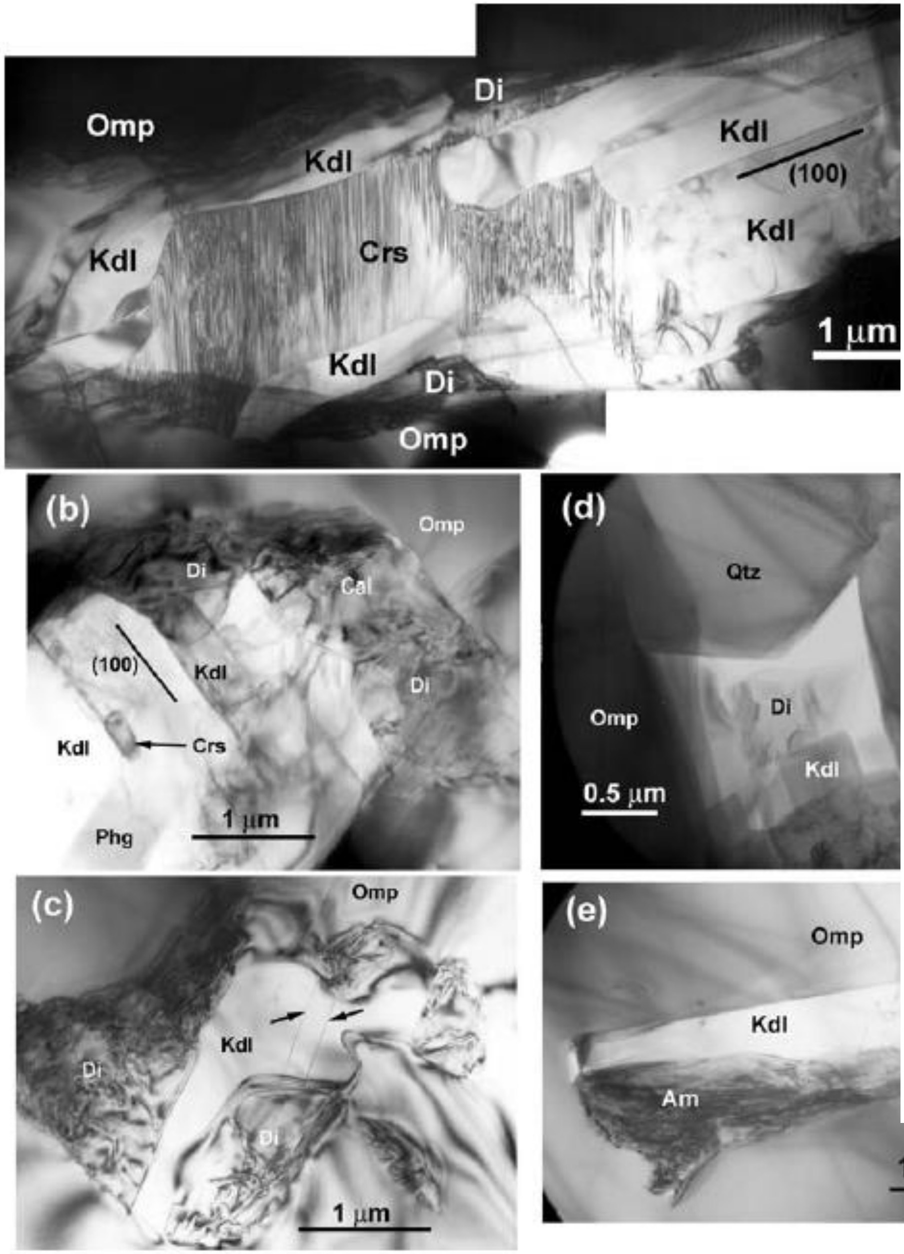
NaAlSi3O8

- Albite
- Triclinic

- Kumdykolite
- Orthorhombic







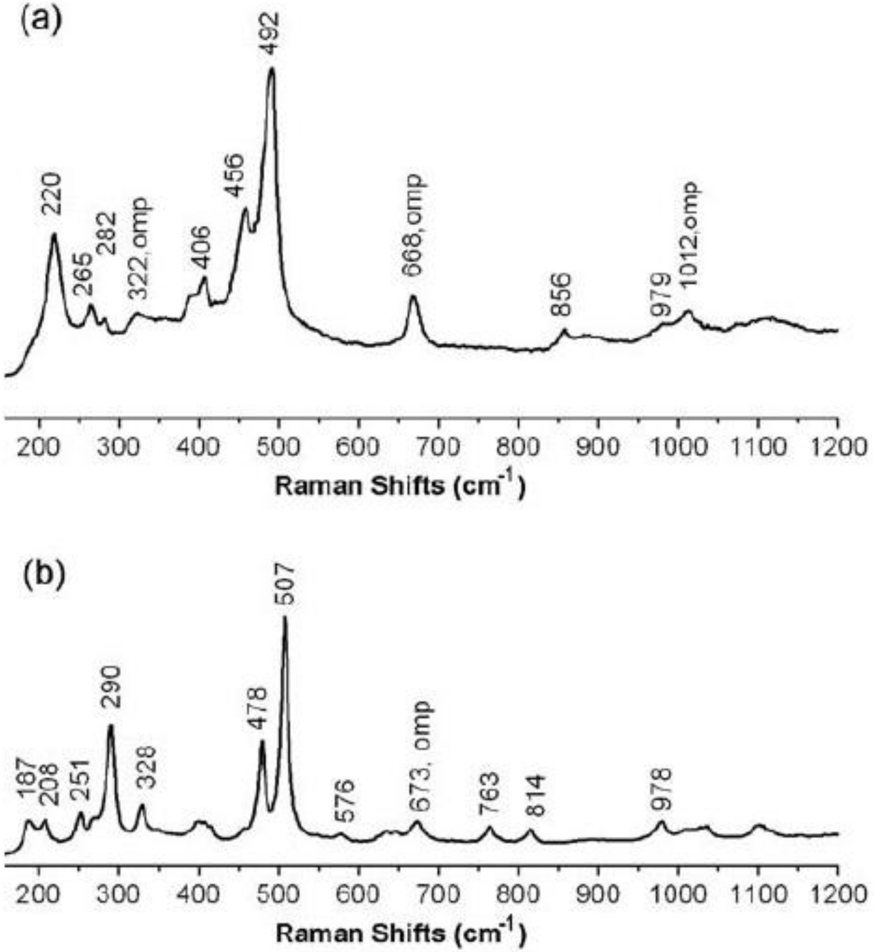
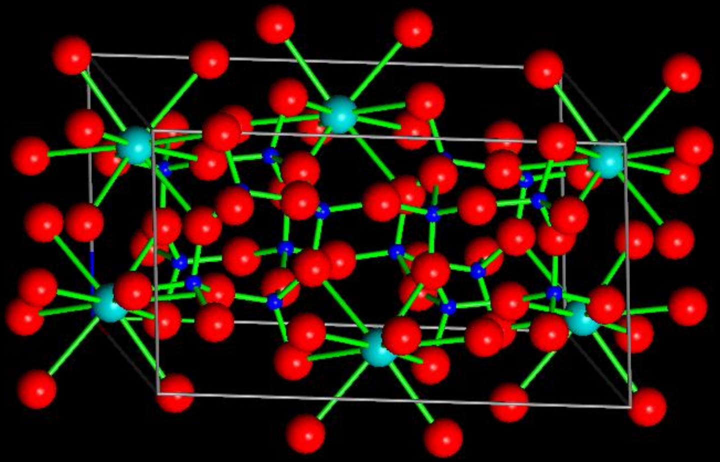


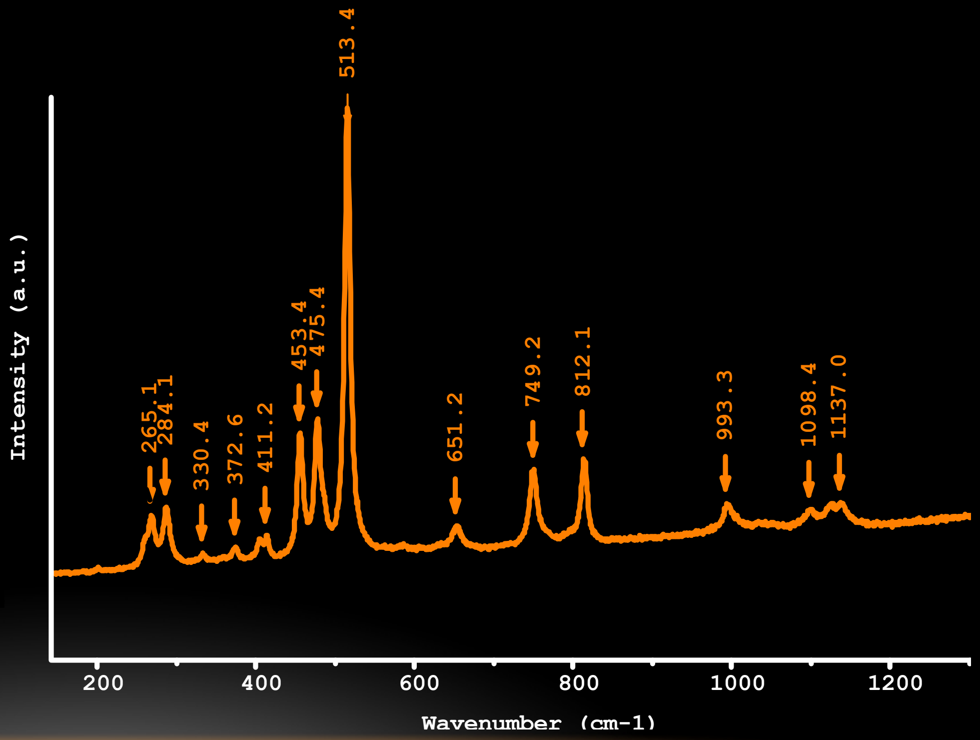
Fig. 4. Raman microprobe spectra of (a) kumdykolite and (b) plagioclase. Additional peaks of omphacite (omp) matrix are also present in (a) and (b).

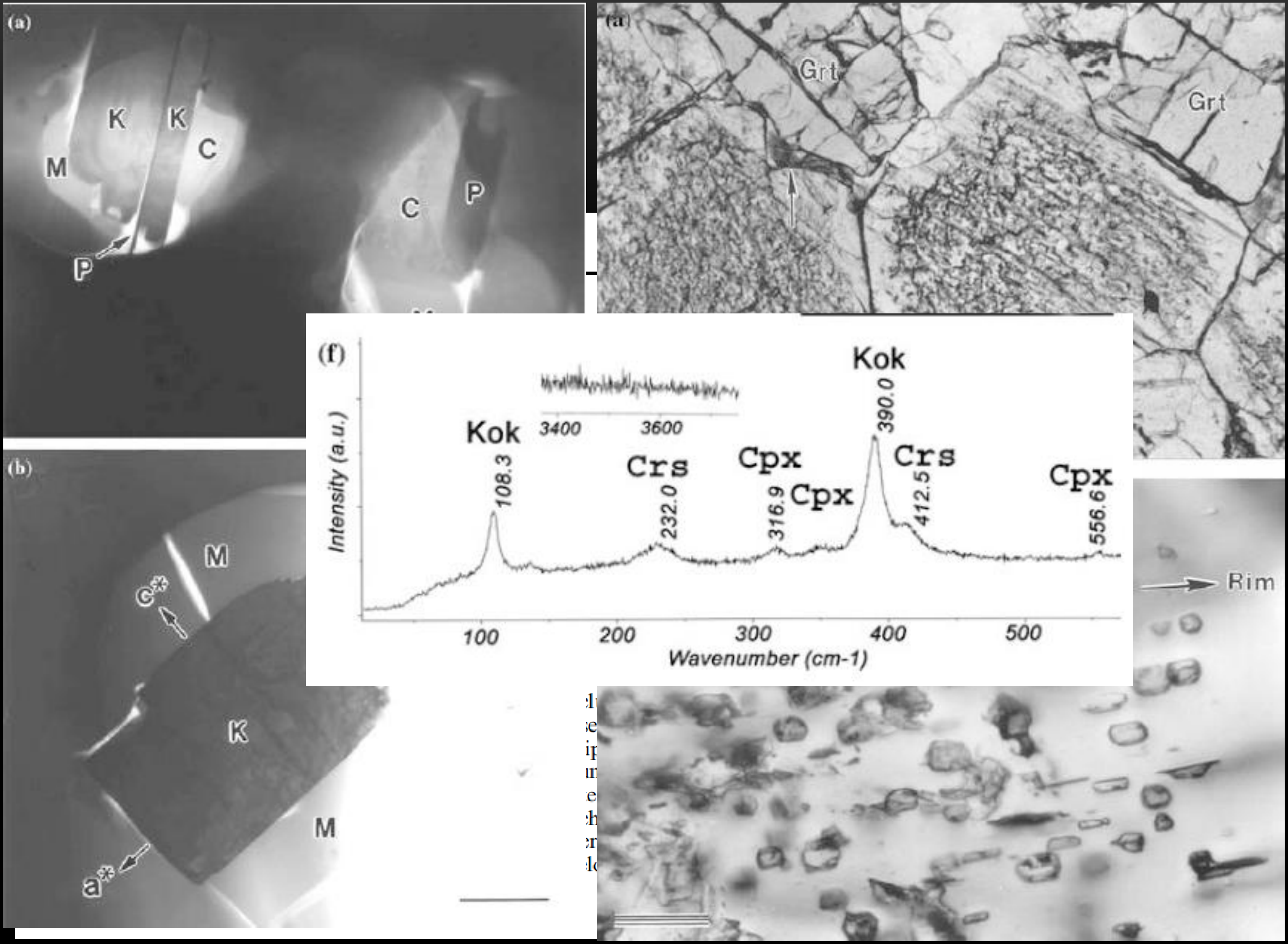
KAlSi3O8

- Orthoclase
- Monoclinic

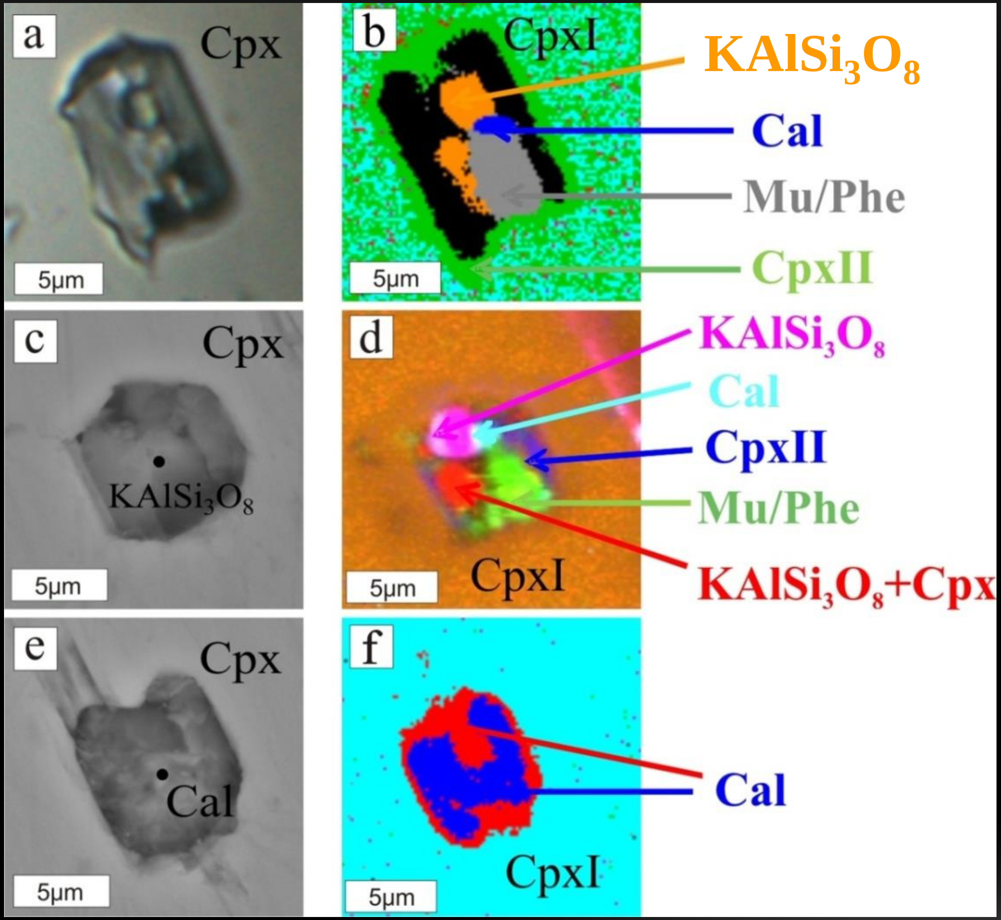
- Kokchetavite
- Hexagonal



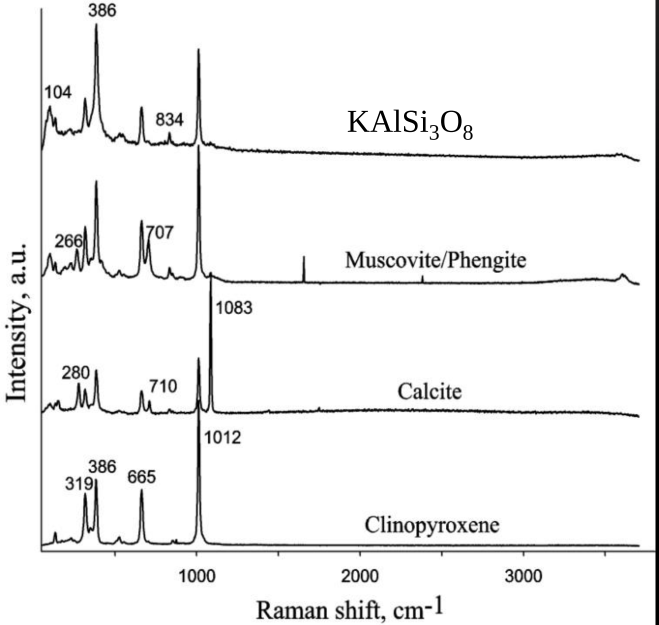



(a)
K
K
C
M
P
C
P
(a)
Grt
Grt
(b)
M
c*
K
M
a*
(f)
Intensity (a.u.)
3400
3600
Kok
108.3
Crs
232.0
Cpx
316.9
Cpx
Kok
390.0
Crs
412.5
Cpx
556.6
100
200
300
400
500
Wavenumber (cm-1)
Rim

Raman imaging on Polyphase inclusions



Polyphase inclusions in Cpx porphyroblast a) transmitted light c),e) SEM images of polyphase inclusions b),d),f) confocal Raman images

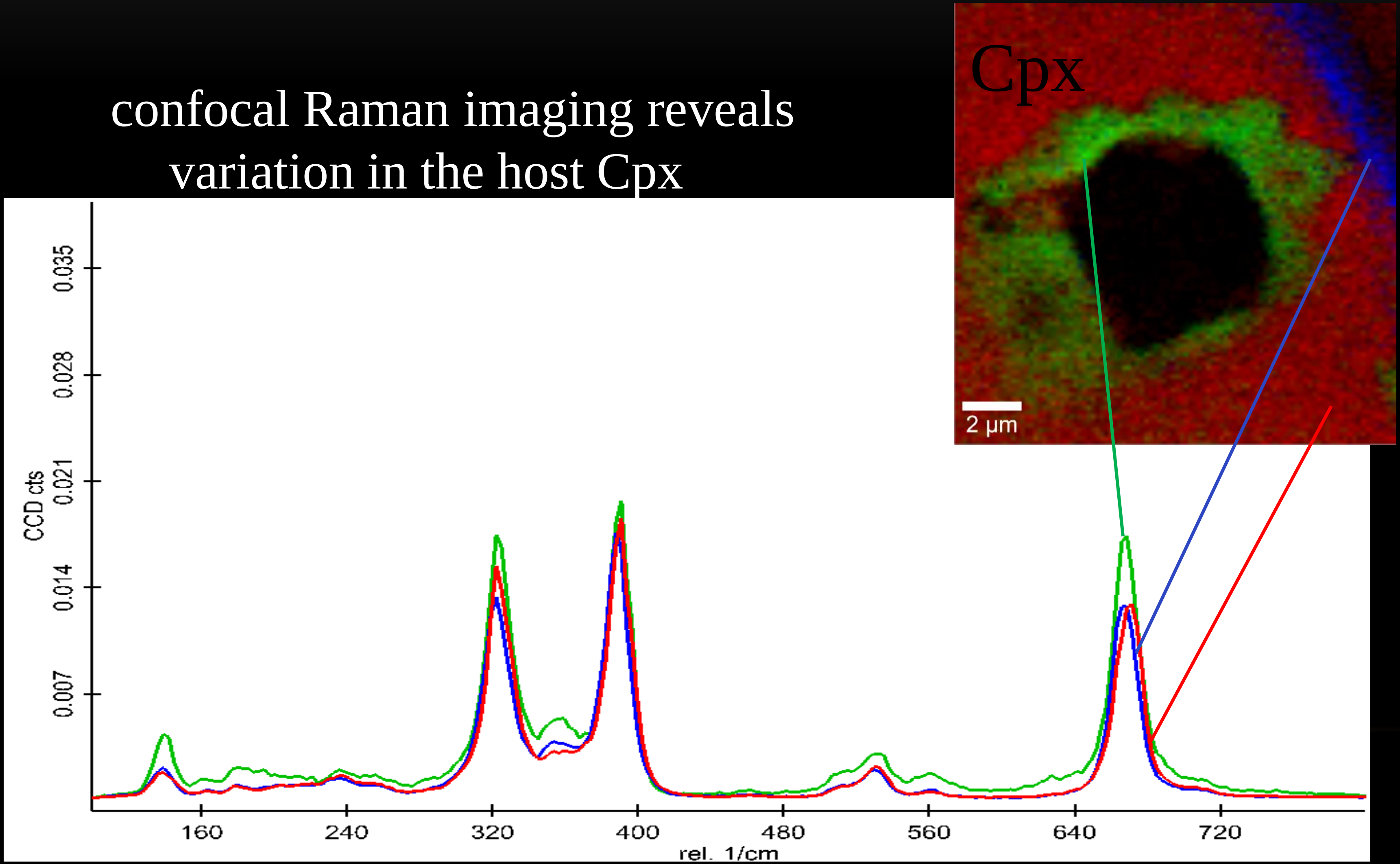


Raman imaging with SEM: identification of Cal, Phe, Hbl, Qtz and $KAlSi_3O_8$ in polyphase inclusions. According to previous studies **these polyphase inclusions represent a melt at peak metamorphic conditions**

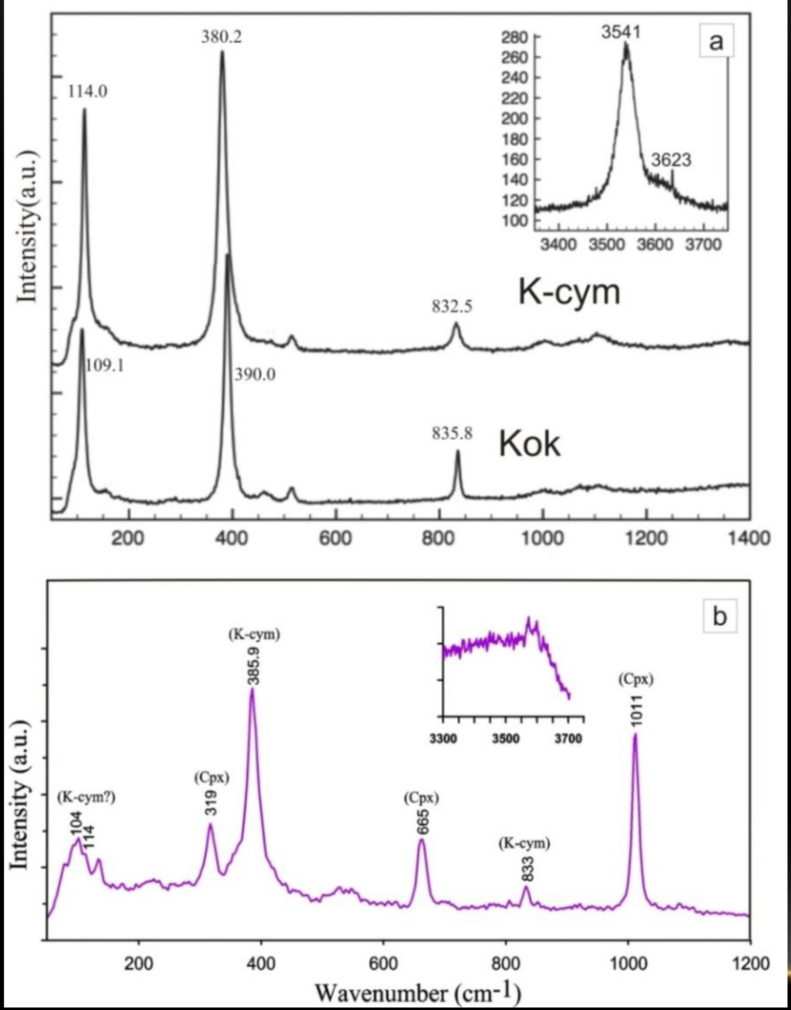
(Perchuk et al., 2004, 2005, 2009; Hwang et al., 2001, 2006; Korsakov&Hermann, 2006)

Raman imaging of polyphase inclusions
(as Fig. c and d before)

confocal Raman imaging reveals variation in the host Cpx



Raman spectra interpretation



a) Raman spectra for K-cymrite and kokchetavite (Kanzaky et al., 2012)
b) Raman spectra of K-cymrite (Mikhno et al., 2013)

- **Raman spectra here** for **KAlSi$_3$O$_8$** show peaks at 102-106 cm^{-1} with a shoulder at 114 cm^{-1}, 385.8 cm^{-1}, 833 cm^{-1} **and OH-stretching** vibration at 3562-3640 cm^{-1}

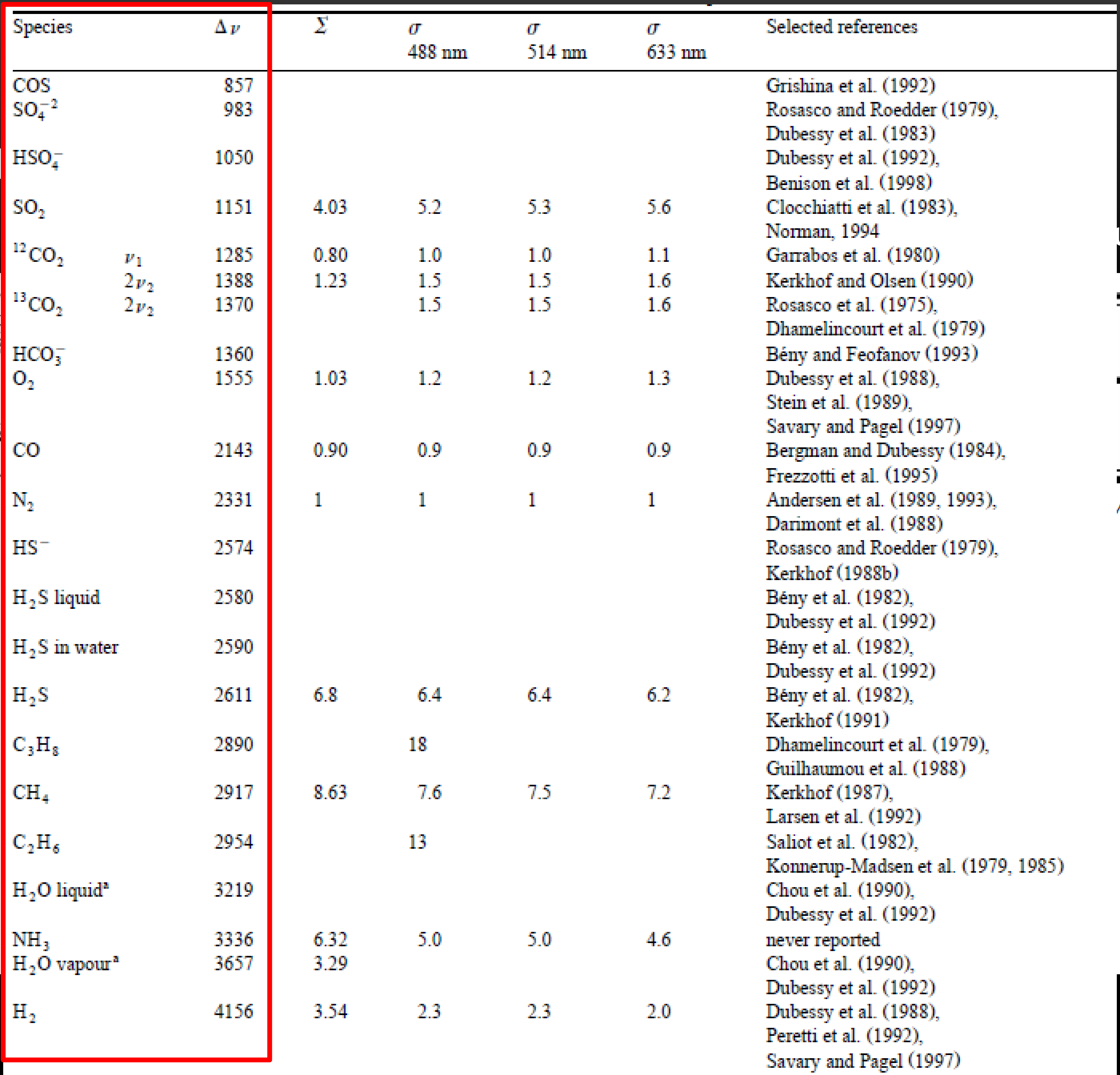
- **A previous Raman** spectroscopic **study** reveals that KAlSi$_3$O$_8$ is predominantly **kokchetavite** (Hwang et al., 2004), which is a **nominally anhydrous** mineral
  → **no OH-stretching mode**.

- **Here:** good **correspondence** for the Raman spectra of **KAlSi$_3$O$_8$** with that of **K-cymrite** (**KAlSi$_3$O$_8$*H_2O**) (major peaks as above and OH-stretching vibration at 3541 cm^{-1} with a shoulder at 3623 cm^{-1}).

→ Therefore we assume that the **observed polyphase inclusions contain K-cymrite**, which was never reported in natural rocks before.

Flu

urface

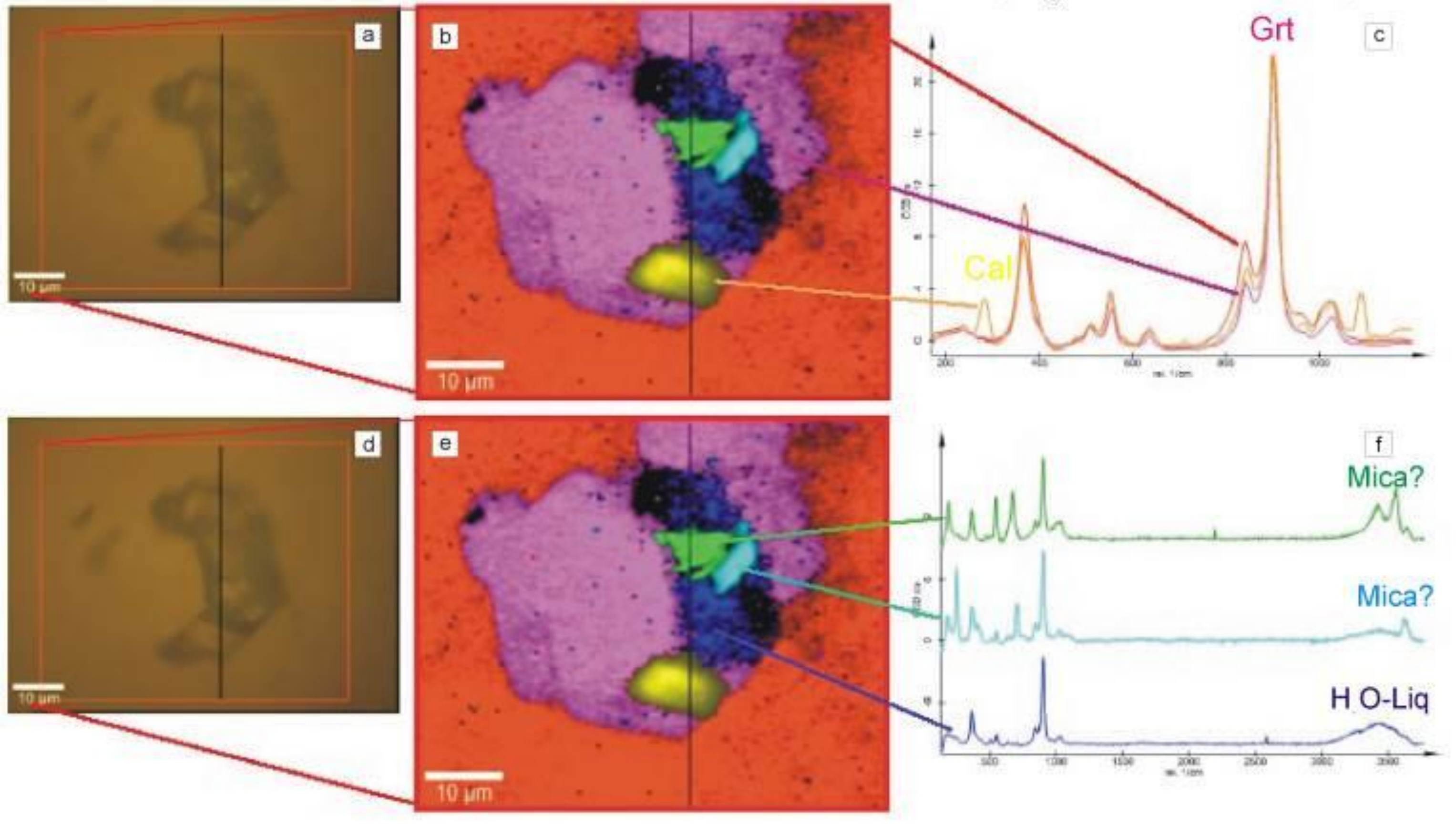


Species		$\Delta\nu$	Σ	σ 488 nm	σ 514 nm	σ 633 nm	Selected references
COS		857					Grishina et al. (1992)
SO_4^{-2}		983					Rosasco and Roedder (1979), Dubessy et al. (1983)
HSO_4^-		1050					Dubessy et al. (1992), Benison et al. (1998)
SO_2		1151	4.03	5.2	5.3	5.6	Clocchiatti et al. (1983), Norman, 1994
$^{12}CO_2$	ν_1	1285	0.80	1.0	1.0	1.1	Garrabos et al. (1980)
	$2\nu_2$	1388	1.23	1.5	1.5	1.6	Kerkhof and Olsen (1990)
$^{13}CO_2$	$2\nu_2$	1370		1.5	1.5	1.6	Rosasco et al. (1975), Dhamelincourt et al. (1979)
HCO_3^-		1360					Bény and Feofanov (1993)
O_2		1555	1.03	1.2	1.2	1.3	Dubessy et al. (1988), Stein et al. (1989), Savary and Pagel (1997)
CO		2143	0.90	0.9	0.9	0.9	Bergman and Dubessy (1984), Frezzotti et al. (1995)
N_2		2331	1	1	1	1	Andersen et al. (1989, 1993), Darimont et al. (1988)
HS^-		2574					Rosasco and Roedder (1979), Kerkhof (1988b)
H_2S liquid		2580					Bény et al. (1982), Dubessy et al. (1992)
H_2S in water		2590					Bény et al. (1982), Dubessy et al. (1992)
H_2S		2611	6.8	6.4	6.4	6.2	Bény et al. (1982), Kerkhof (1991)
C_3H_8		2890		18			Dhamelincourt et al. (1979), Guilhaumou et al. (1988)
CH_4		2917	8.63	7.6	7.5	7.2	Kerkhof (1987), Larsen et al. (1992)
C_2H_6		2954		13			Saliot et al. (1982), Konnerup-Madsen et al. (1979, 1985)
H_2O liquid[a]		3219					Chou et al. (1990), Dubessy et al. (1992)
NH_3		3336	6.32	5.0	5.0	4.6	never reported
H_2O vapour[a]		3657	3.29				Chou et al. (1990), Dubessy et al. (1992)
H_2		4156	3.54	2.3	2.3	2.0	Dubessy et al. (1988), Peretti et al. (1992), Savary and Pagel (1997)

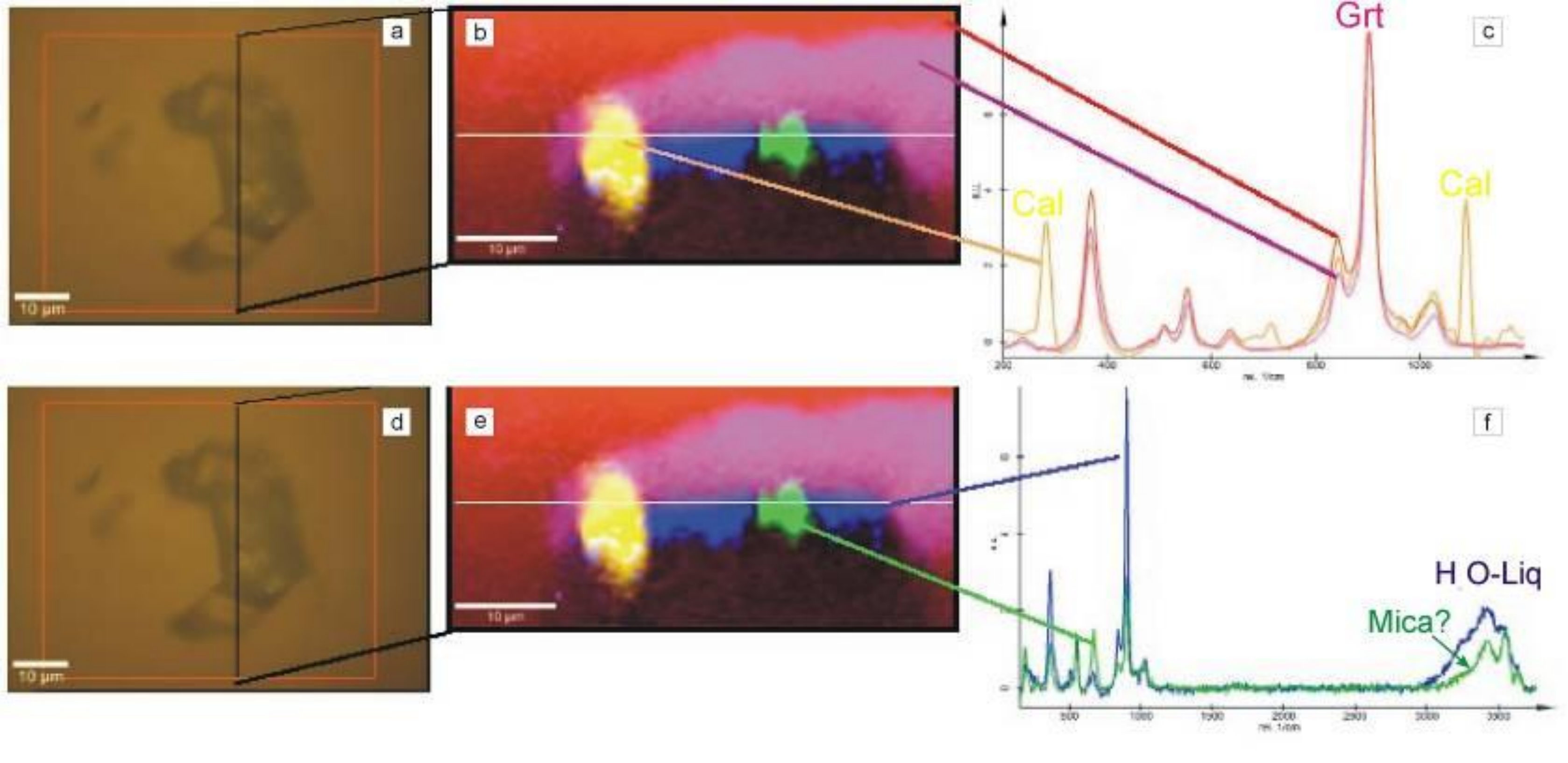
ELSEVIER

HOS

/locate/lithos



- XY Raman Image of the inclusion. The Raman spectra of the garnet show some significant variations in the relative peak intensities (c). The spectra shown above are normalize to the peak near 900 cm^{-1} and the differences are clearly visible between the red and the magenta spectra (especially from the peak near 850 cm-1 and near 360 cm^{-1}; here the magenta curve is overlapped by the orange curve). The orange spectra shows the calcite. The aqueous phase showed some significant differentiation, which can clearly be seen from the spectra shown on the right (f). Cal=calcite, H_2O-Liq= liquid water, Grt=garnet

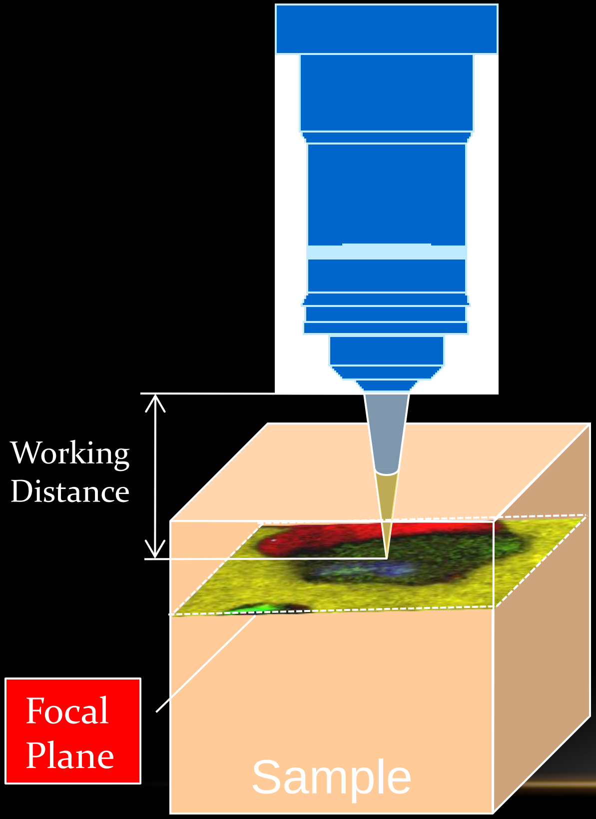


- In the YZ (Depth) Scan, the Garnet signal again shows some significant variations in the relative peak intensities. The spectra shown above are normalize to the peak near 900 cm^{-1} and the differences are clearly visible between the red and the magenta spectra (especially from the peak near 850 cm^{-1} and near 360 cm^{-1}). It seems as if the magenta phase is lying in between the red garnet phase and the aqueous phase.

Confocal Raman Imaging of inclusions: the principle

3D-Raman : confocality at the diffraction limit

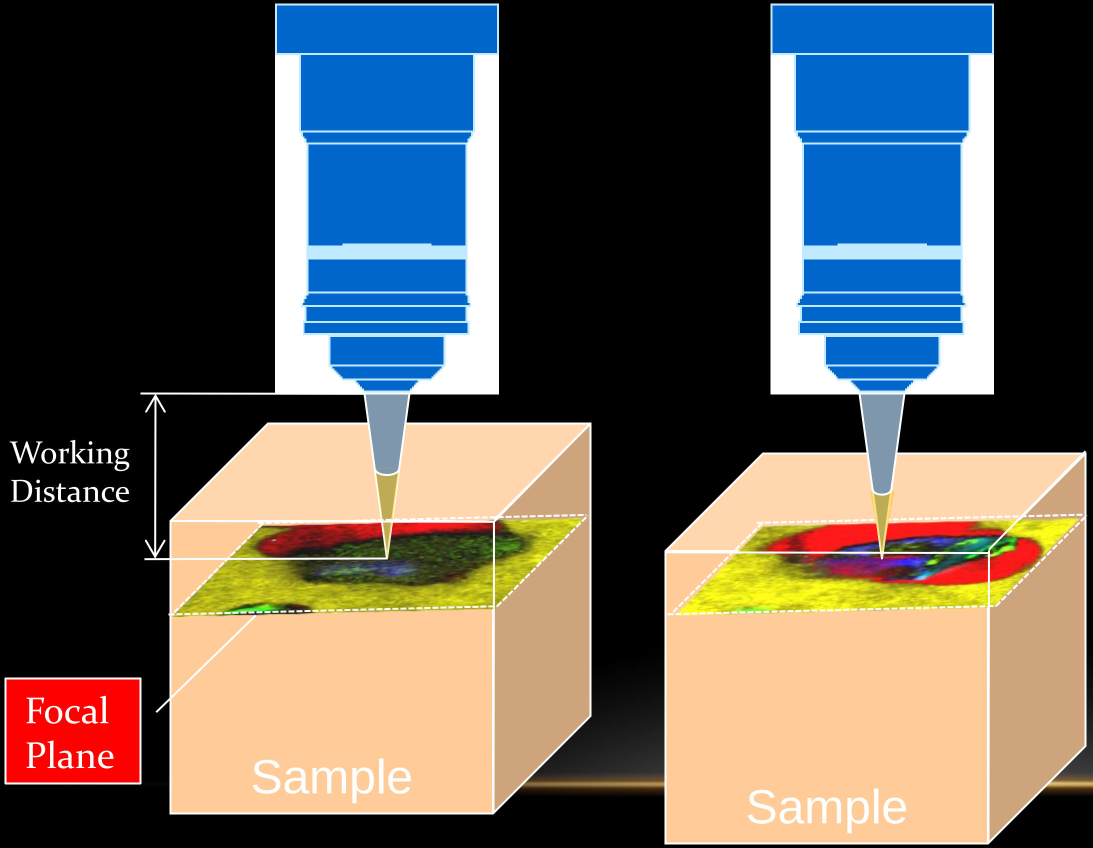
→ x-y resolution ~350nm, z resolution ~850nm



Confocal Raman Imaging of inclusions: the principle

3D-Raman : confocality at the diffraction limit

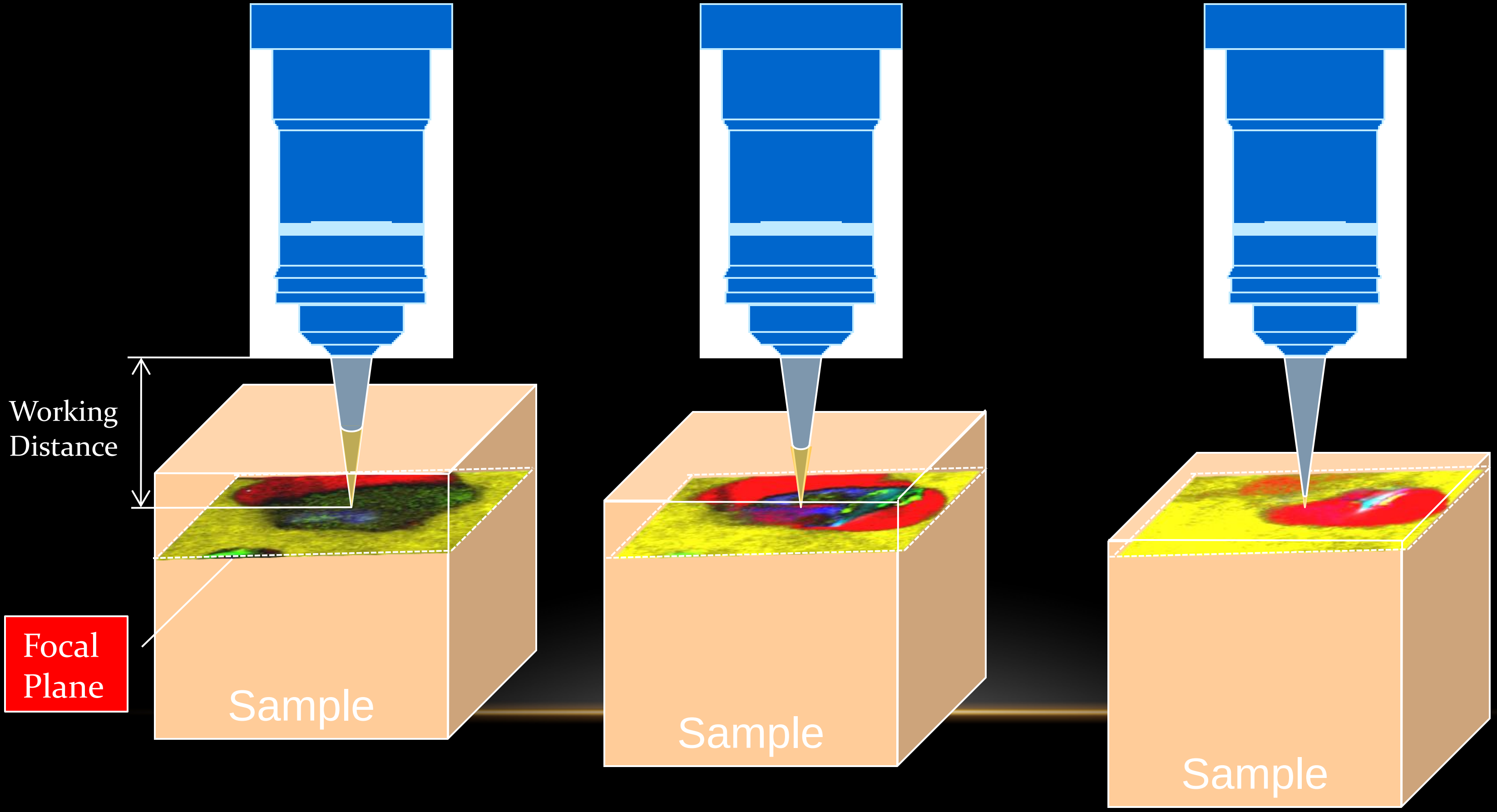
→ x-y resolution ~350nm, z resolution ~850nm



Confocal Raman Imaging of inclusions: the principle

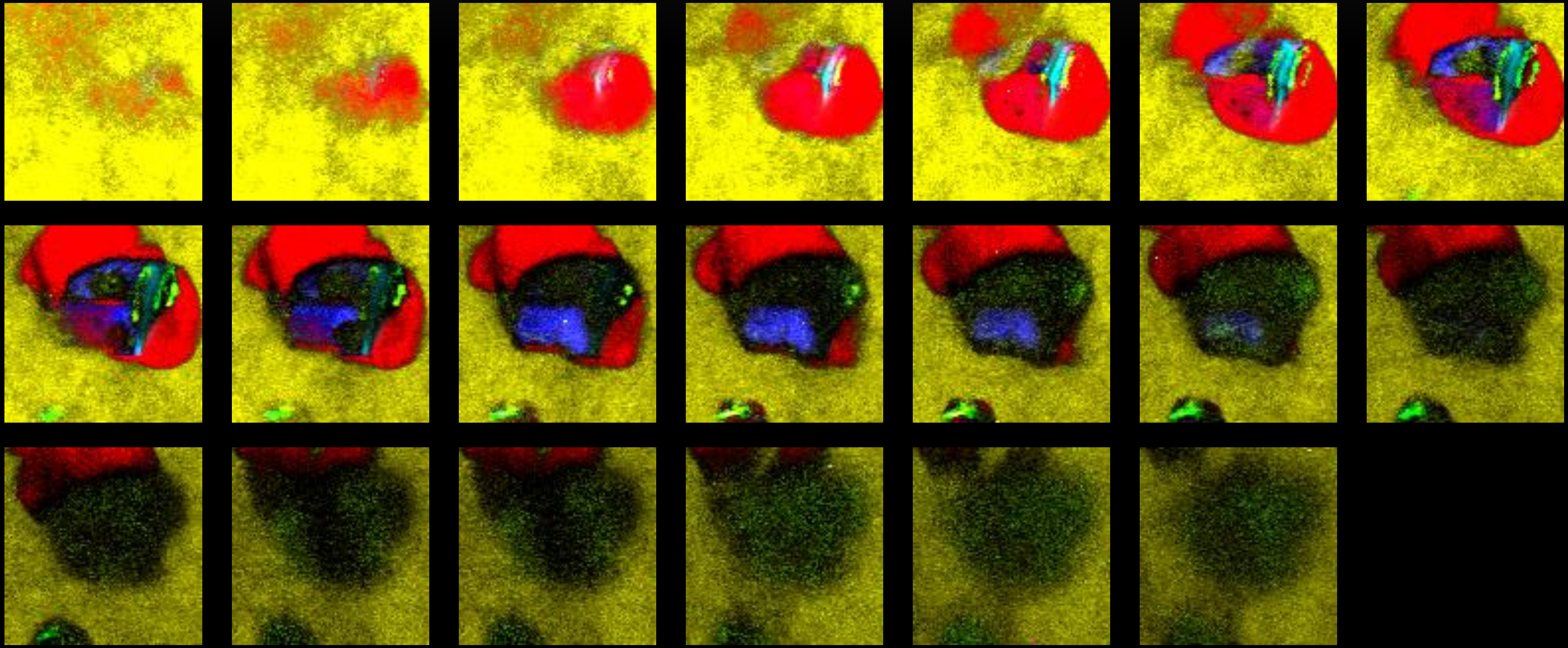
3D-Raman : confocality at the diffraction limit

→ x-y resolution ~350nm, z resolution ~850nm



Confocal Raman Imaging

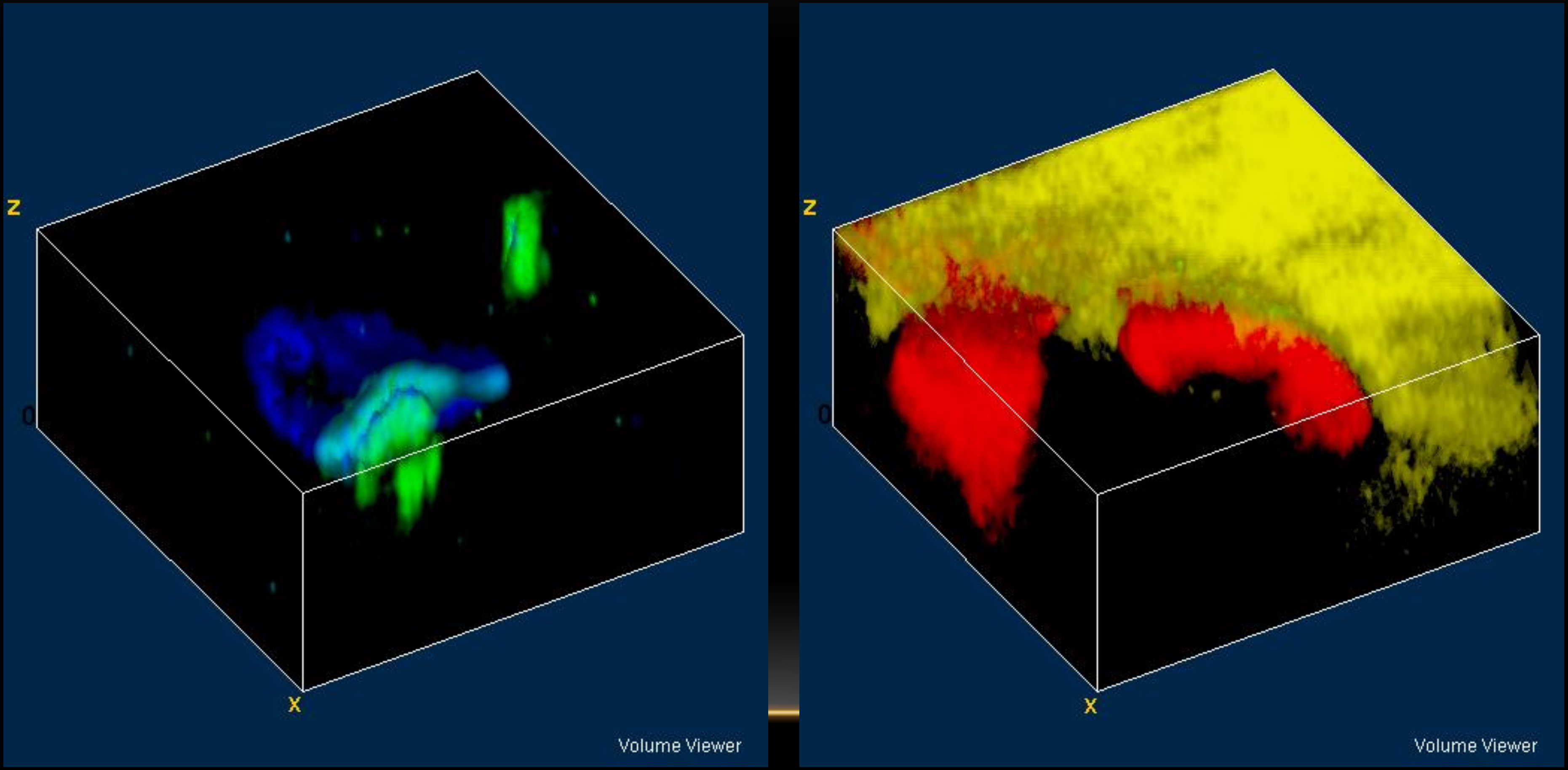
3D-Raman : polyphase inclusion in Garnet



100 x 100 x 20 (=200,000) spectra
0.132s integration time per spectrum
60 x 60 x 30 µm^3
532 nm excitation; 100x NA=0.9

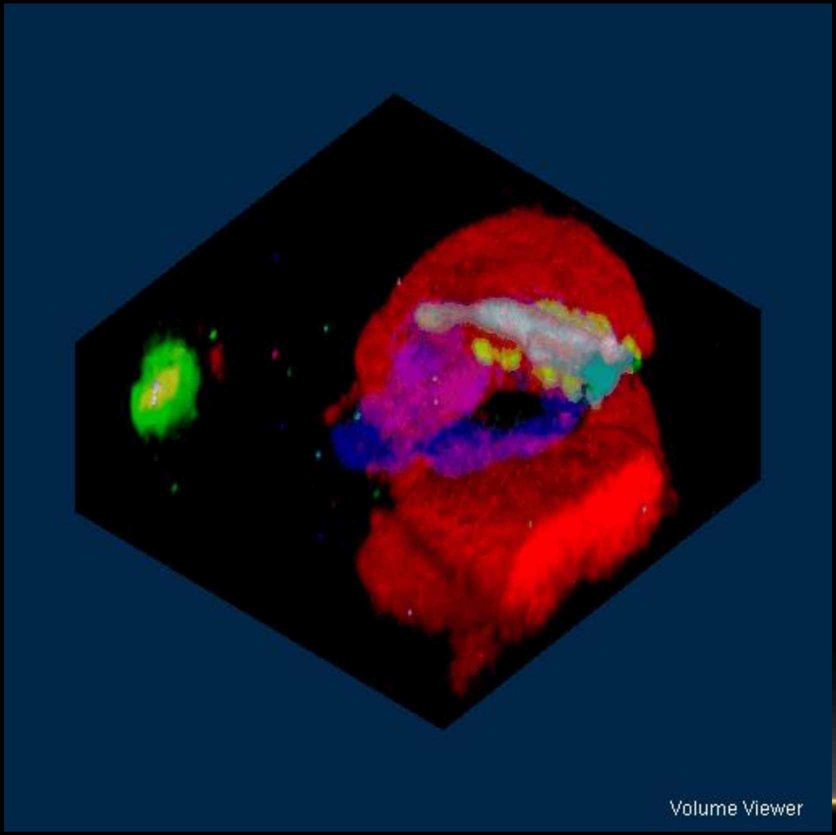
Confocal Raman Imaging

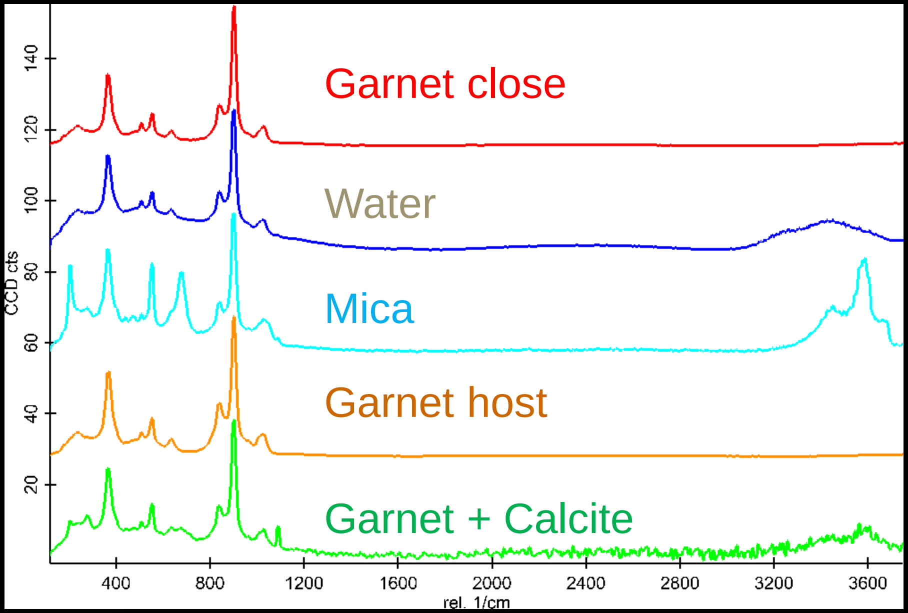
3D-Raman : polyphase inclusion in Garnet



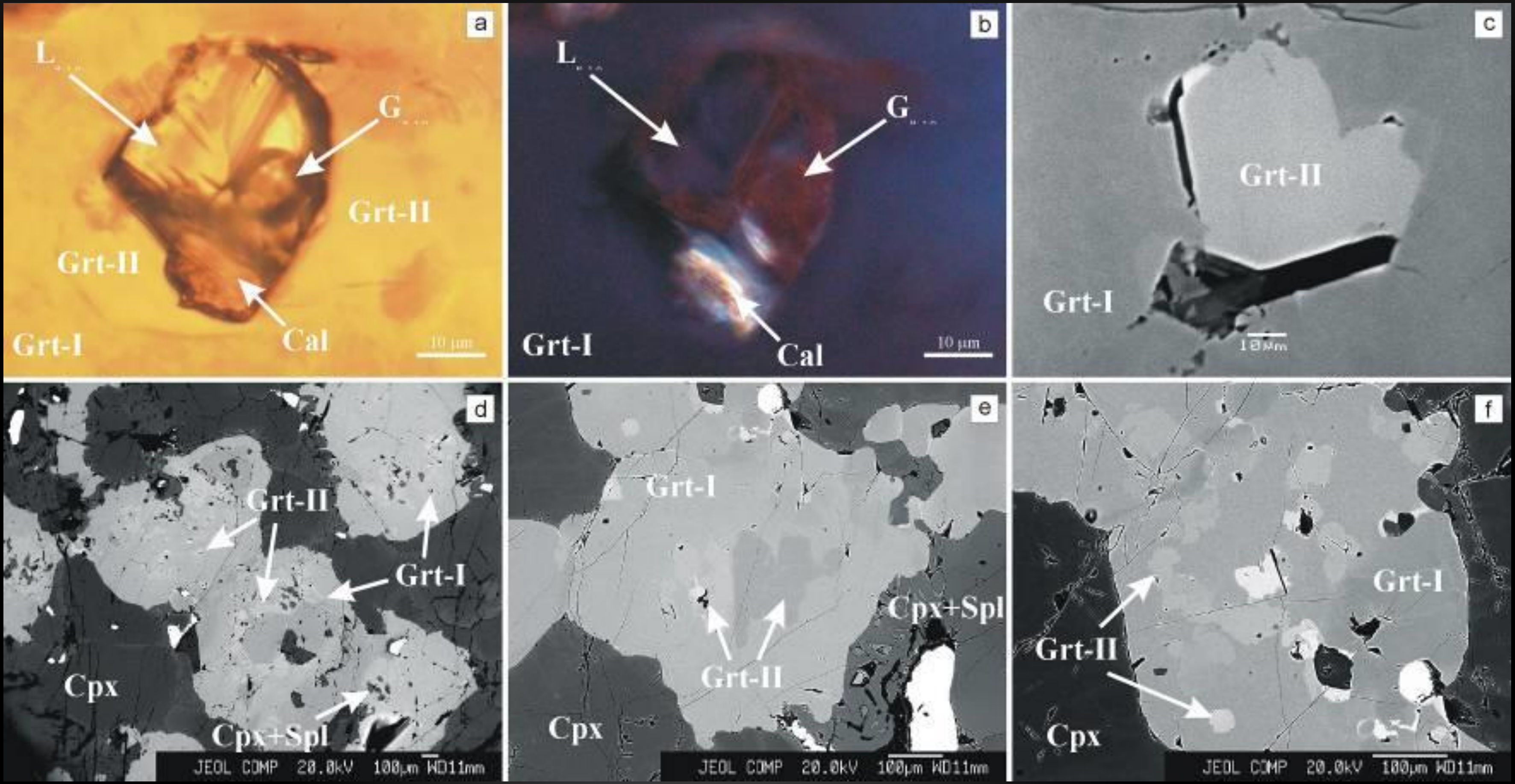
Confocal Raman Imaging

3D-Raman : polyphase inclusion in Garnet





BSE-images



Garnet compositions: $Alm_{22-23}Sps_{2.1-2.3}Pyr_{22-24}Grs_{51-52}$ (Grt-I) and $Alm_{20-27}Sps_{2.0-3.8}Pyr_{7-27}Grs_{50-62}$ (Grt-II)

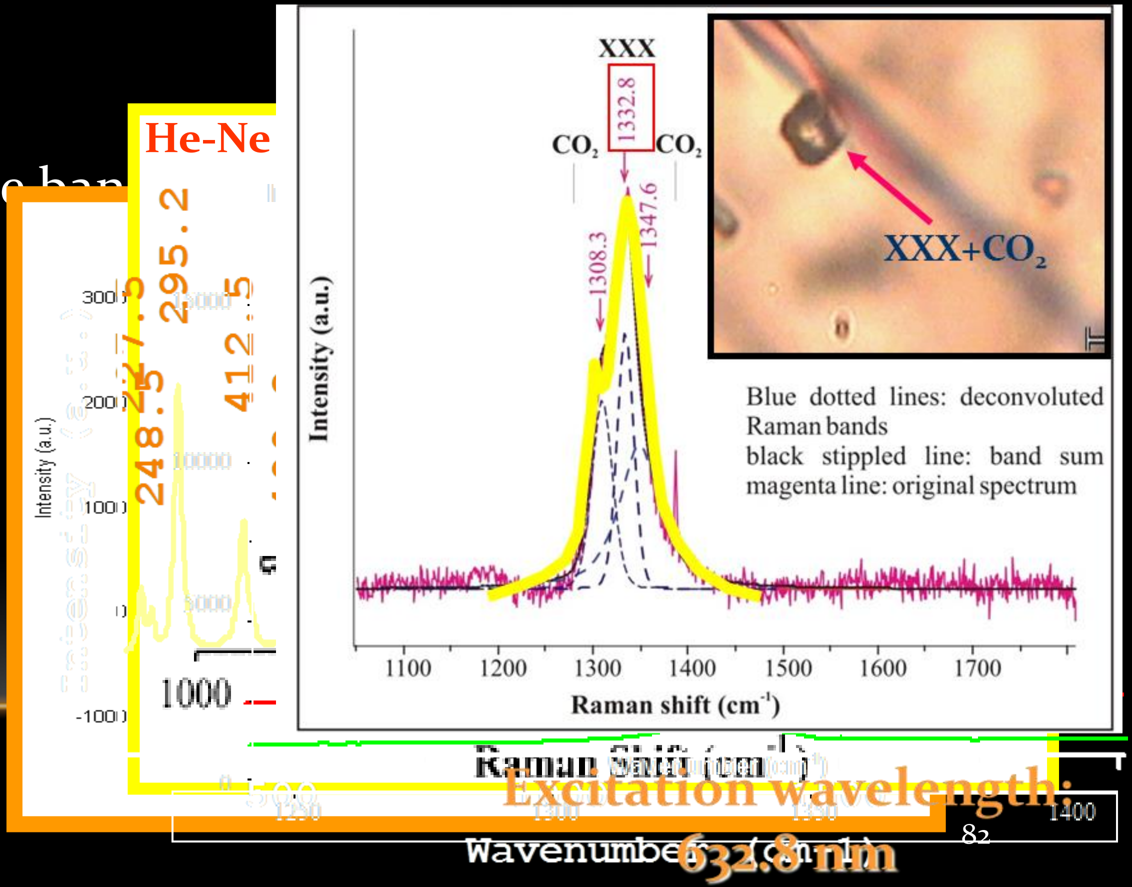
Tips & Advice

- Acquire a spectrum of the host mineral first
  - Garnet
  - Pyroxene
  - Zircon
  - Micas
  - Titanite
  - Rutile
  - …

Tips & Advice

- **Acquire a spectrum of the host mineral first**
- **Acquire the whole spectral region** (surprise might be hidden)

- A band at ~1330 cm^{-1}
  - The F2g diamond band
  - The D1 (disorder) graphite ban
  - Lonsdaleite band
  - Haematite band
  - XXX luminescence band



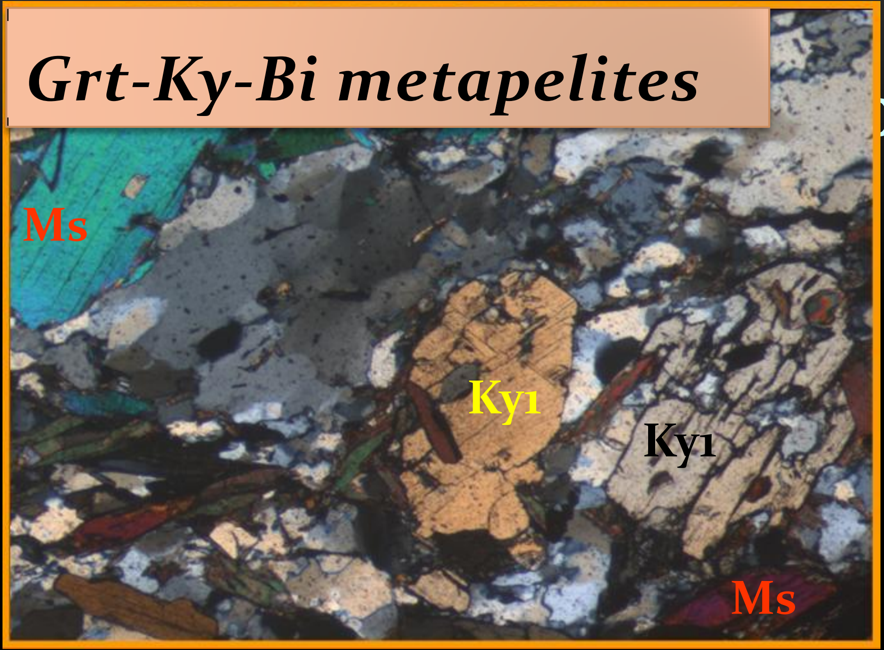
Tips & Advice

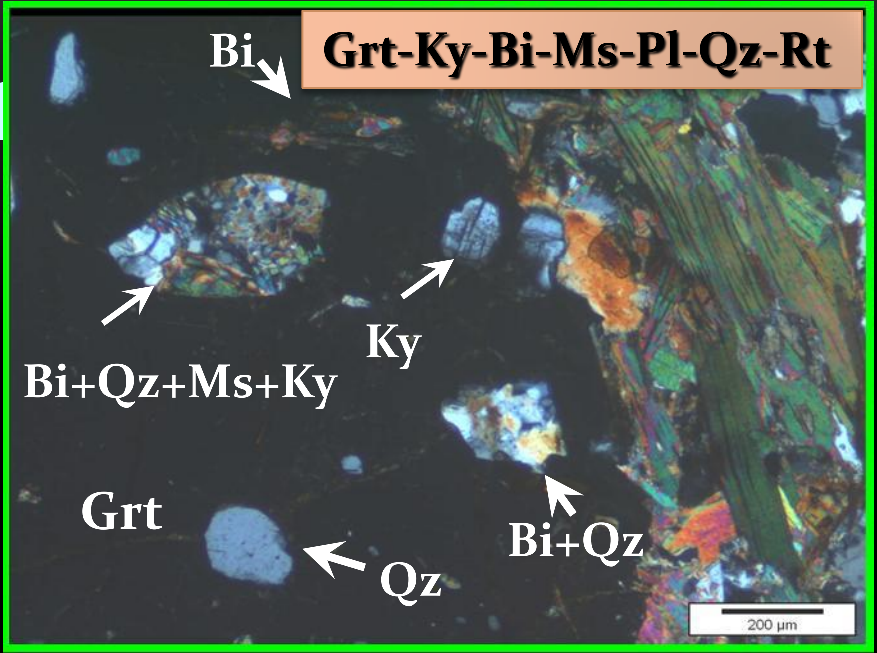
- **Acquire a spectrum of the host mineral first**
- **Acquire the whole spectral region**
- **Never underestimate band (up-/down-) shifts or significant band broadening**
- **Pay attention to extra peaks**
- **Multi-wavelength laser analysis if possible (be careful of laser-induced artifacts e.g. luminescence bands)**

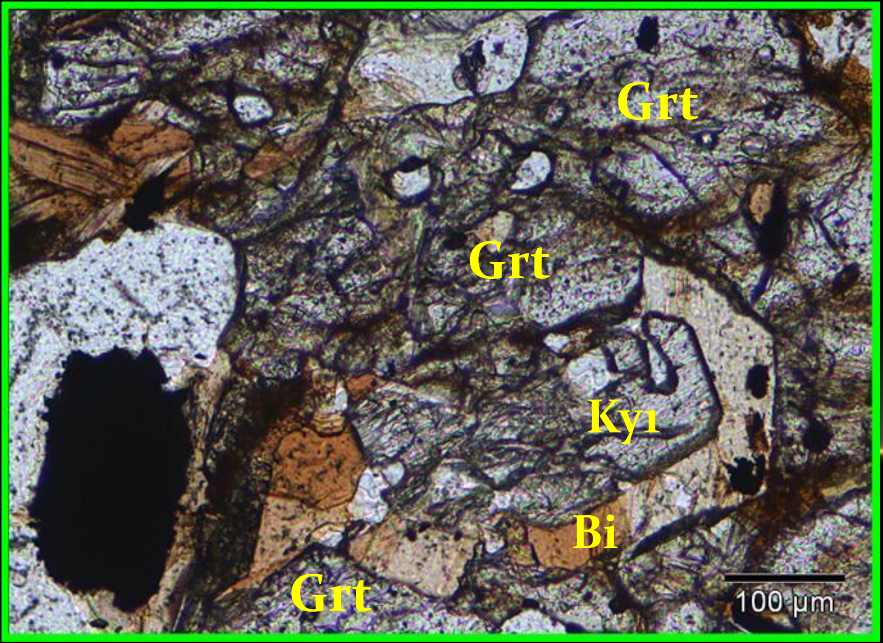
Raman Spectroscopy : A powerful tool in studying metamorphic rocks

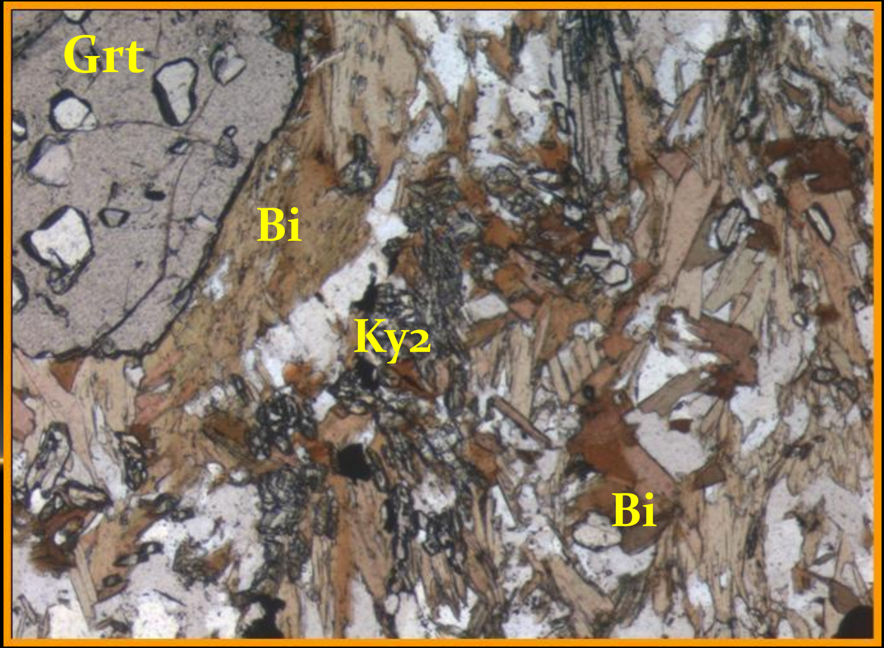
As it converts …

Grt-Ky-Bi metapelites

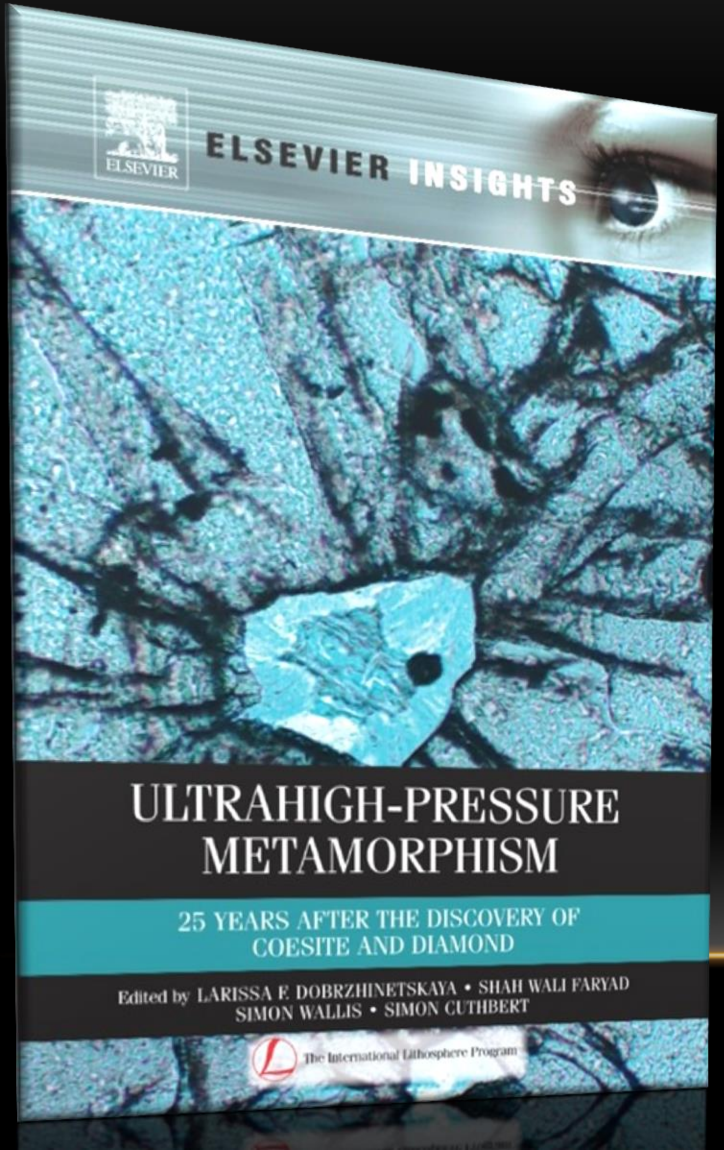



Grt-Ky-Bi-Ms-Pl-Qz-Rt





…to spectacular discoveries



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ULTRAHIGH-PRESSURE METAMORPHISM

25 YEARS AFTER THE DISCOVERY OF COESITE AND DIAMOND

Edited by LARISSA F. DOBRZHINETSKAYA • SHAH WALI FARYAD
SIMON WALLIS • SIMON CUTHBERT

The International Lithosphere Program

Спасибо!