Gemology workshop
24th January 2014

Institut de recherche pour le développement

GÉOSCIENCES ENVIRONNEMENT TOULOUSE

Isotopic signatures and fluid inclusions in emerald and corundum regarding their geological origin

Gaston Giuliani

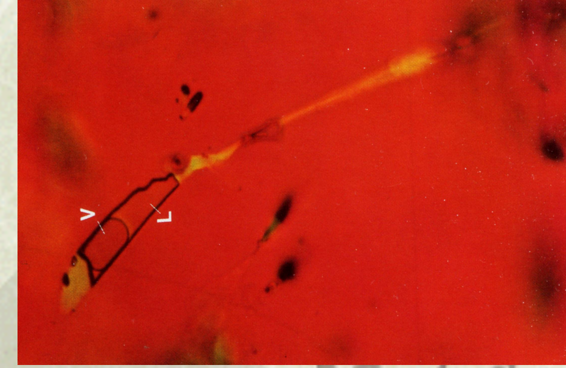
C R P G

UNIVERSITÉ DE LORRAINE

University of Geneva


Trapiche ruby


Mong Hsu ruby


Fluid inclusion in ruby

Outline of the conference

1 - Emerald and corundum: an outline

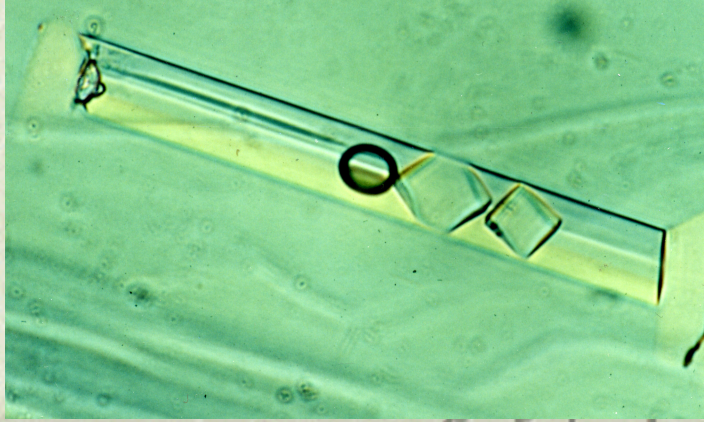
2 - Age correlation of gems and tectono-magmatic events

3 - Genesis of the main economic types of emerald and Corundum deposits

4 - Conclusions


Emerald trapiche

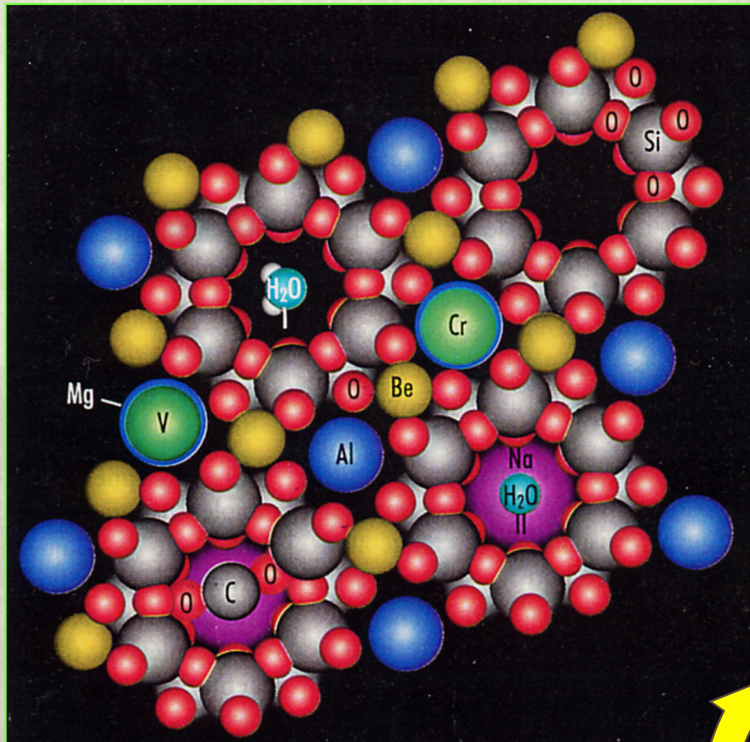

Colombian emerald

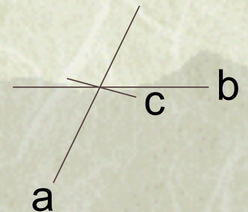

Colombian three-phase fluid inclusion

1

Emerald and corundum: an outline

Emerald: Queen of the beryl family






(Extra Lapis, 2002)

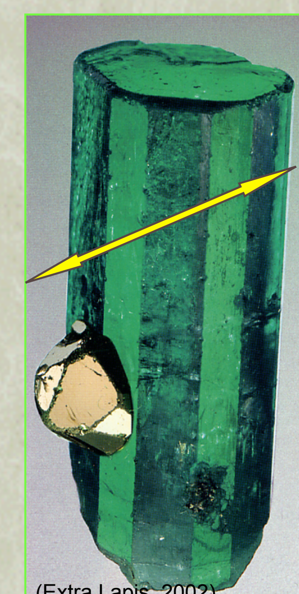
$x = Be_3\ Al_2\ Si_6\ O_{18}$ (Cr-V-Fe-Mg)

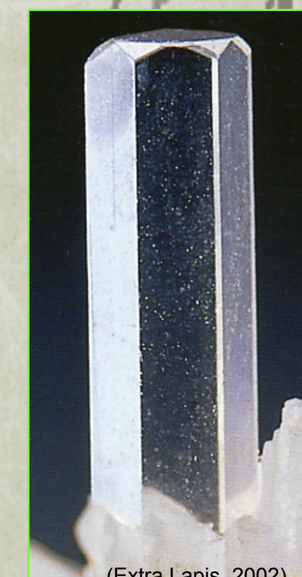
or

$3\ BeO + Al_2O_3 + 6\ SiO_2$

14% 19% 67%

Channels forming Si_6O_{18} rings connected by two octahedrons Al^{VI} and three tetrahedrons Be^{4+}


(Extra Lapis, 2002)


(Extra Lapis, 2002)

Cyclosilicates Group

The corundum family

Aluminium oxide (Al_2O_3)

Cr^{3+}, V^{3+}

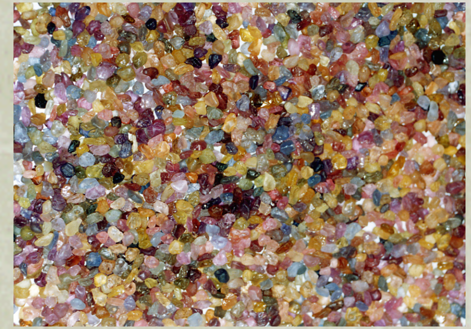
Substitution octahedral site

(Fe, Ti, Mg), Fe -O- Ti

Fe^{2+} -O- Ti^{4+}

Intervalence charge transfert

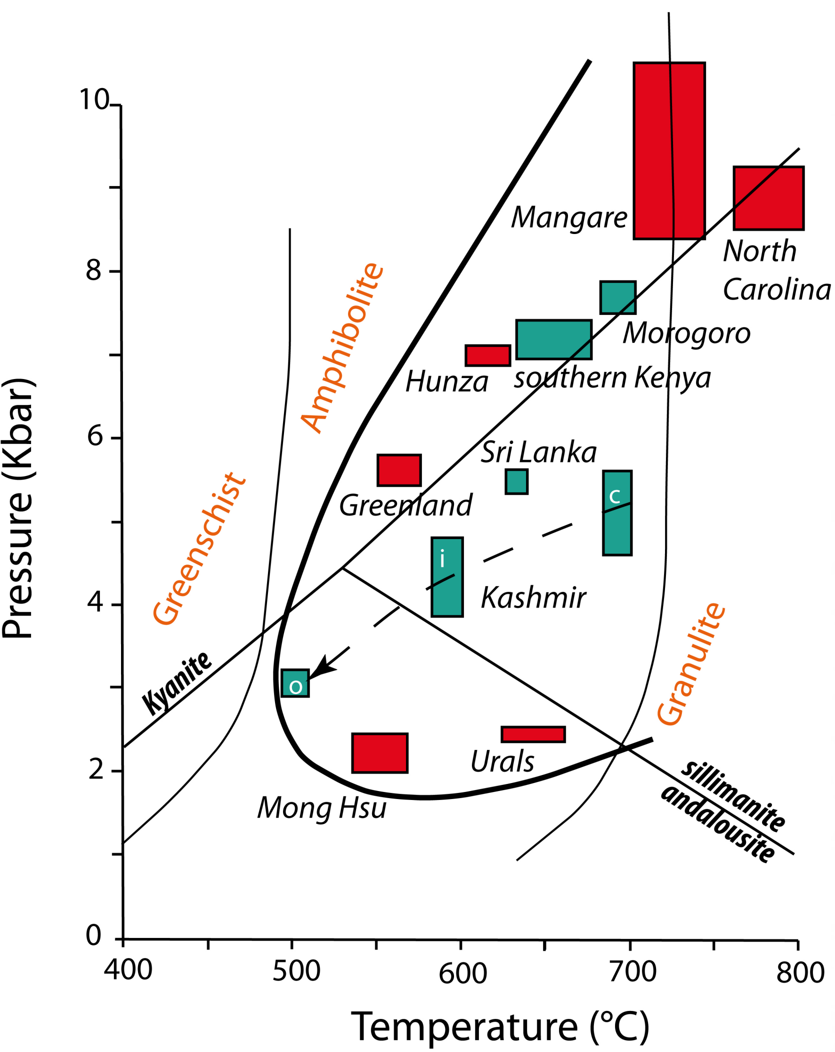
Sapphire is the specific blue corundum variety



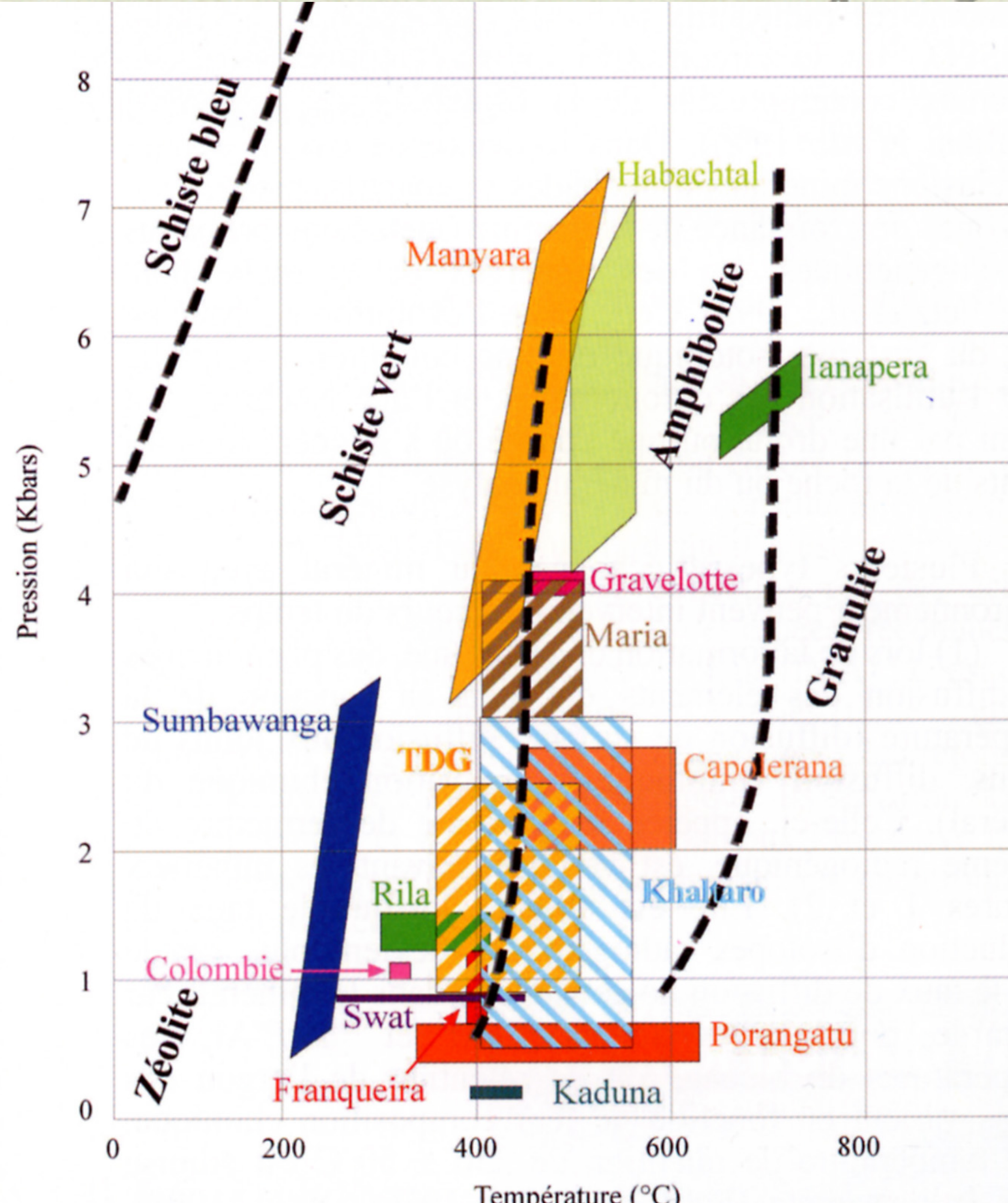
The coloured sapphires are the other types of corundum

Ruby is the specific red variety of corundum

Summary of available data on P-T conditions for emerald and corundum gem deposits

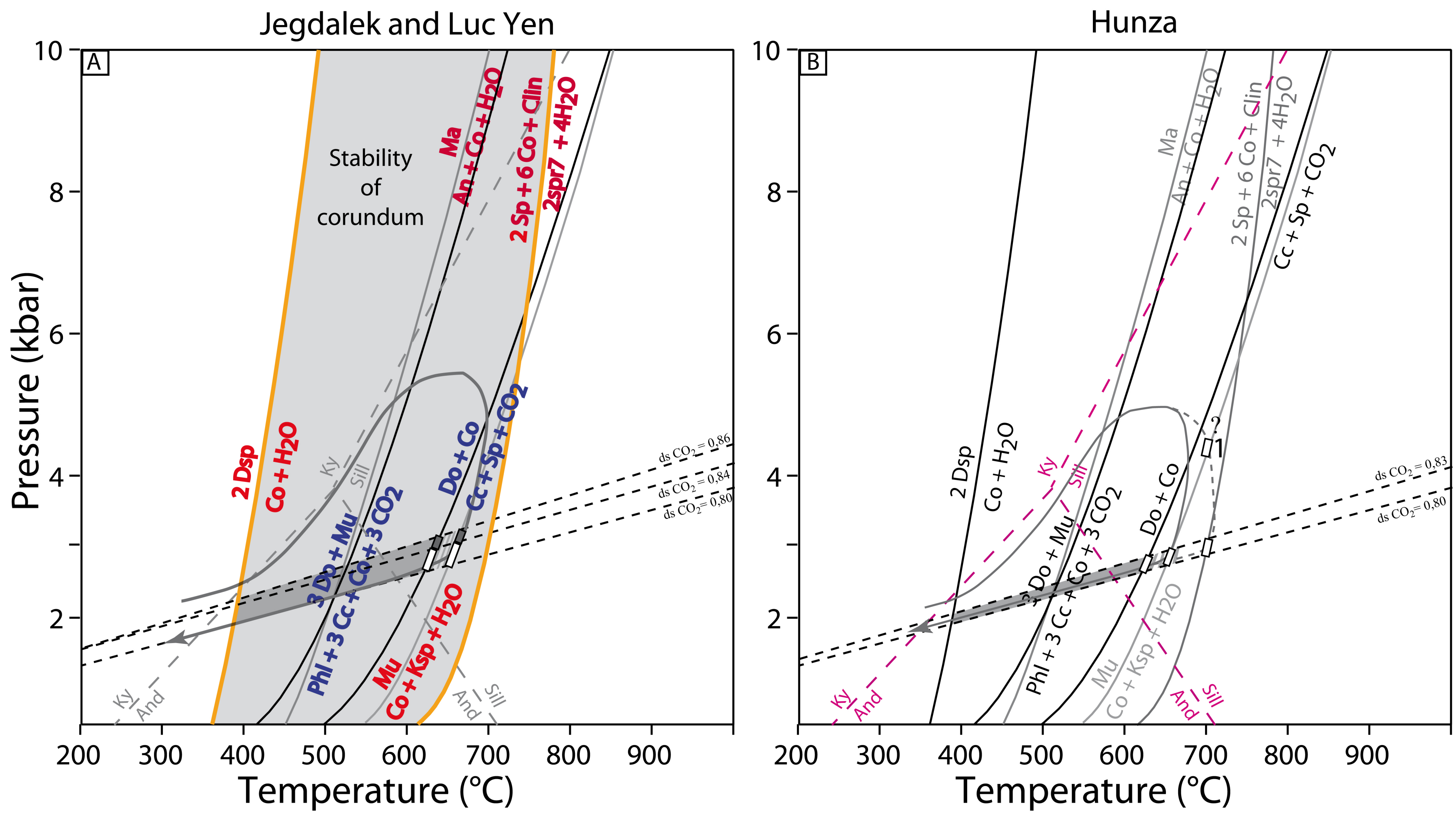


Simonet (2008)



Giuliani (2011)

P-T conditions of stability for mineral associations from ruby-bearing marbles



Conditions of gem ruby crystallisation in Afghanistan

Conditions of gem ruby crystallisation in Vietnam

Domain of ruby stability in marbles

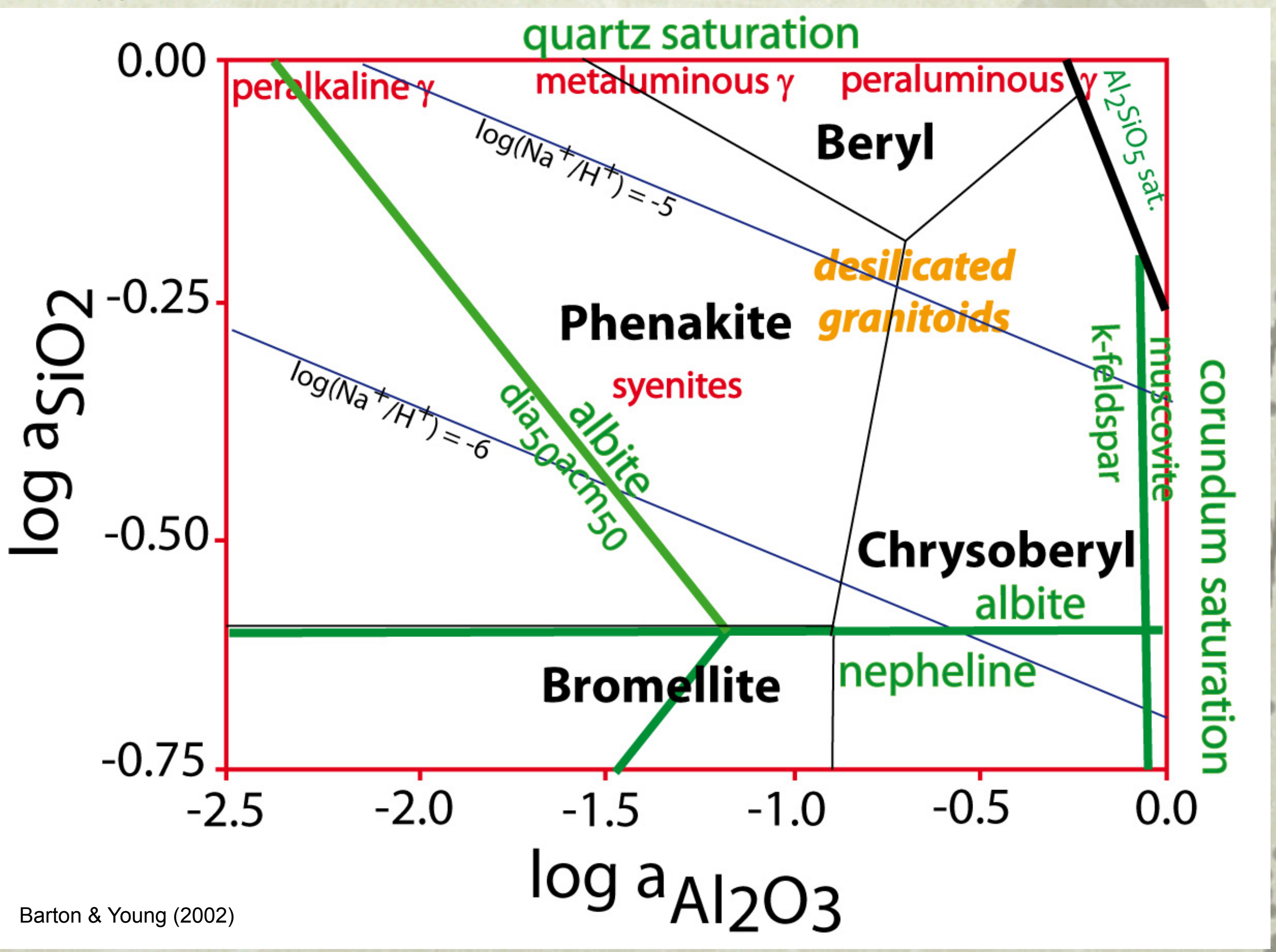
Isochores of fluid inclusions trapped in gem ruby

Conditions of gem ruby crystallisation

Garnier et al. (2008)

Be- mineral stabilities as a function of silica and alumina activities

T= 600°C et P= 1 kbar



alexandrite + phenakite + $5H_4SiO_2$ → emerald + 10 H_2O

(Be_2SiO_4)

Fluid inclusions, stable isotopes and noble gases

Fluid inclusions study using microthermometry, Raman micro-spectrometry, Scanning Electron Microprobe, Infra-red spectrometry, crushing and analysis of cations and anions, ICP-MS laser ablation,

Stable isotopes such as O, H, C, S, B

Noble gases such as He, Ne, Xe, Ar

The use of stable isotopes on the example of oxygen

Emerald : ~ 45 wt% ; Ruby and sapphire : ~ 45 wt% ;
Tsavorite : ~ 42 wt% ; Tanzanite : ~ 46% wt%

3 isotopes of oxygen: ^{16}O, ^{17}O and ^{18}O

$^{18}O/^{16}O = 2.0052 \times 10^{-3}$

(for 1 atom of ^{18}O, there are more os less 498,7 atoms of ^{16}O)

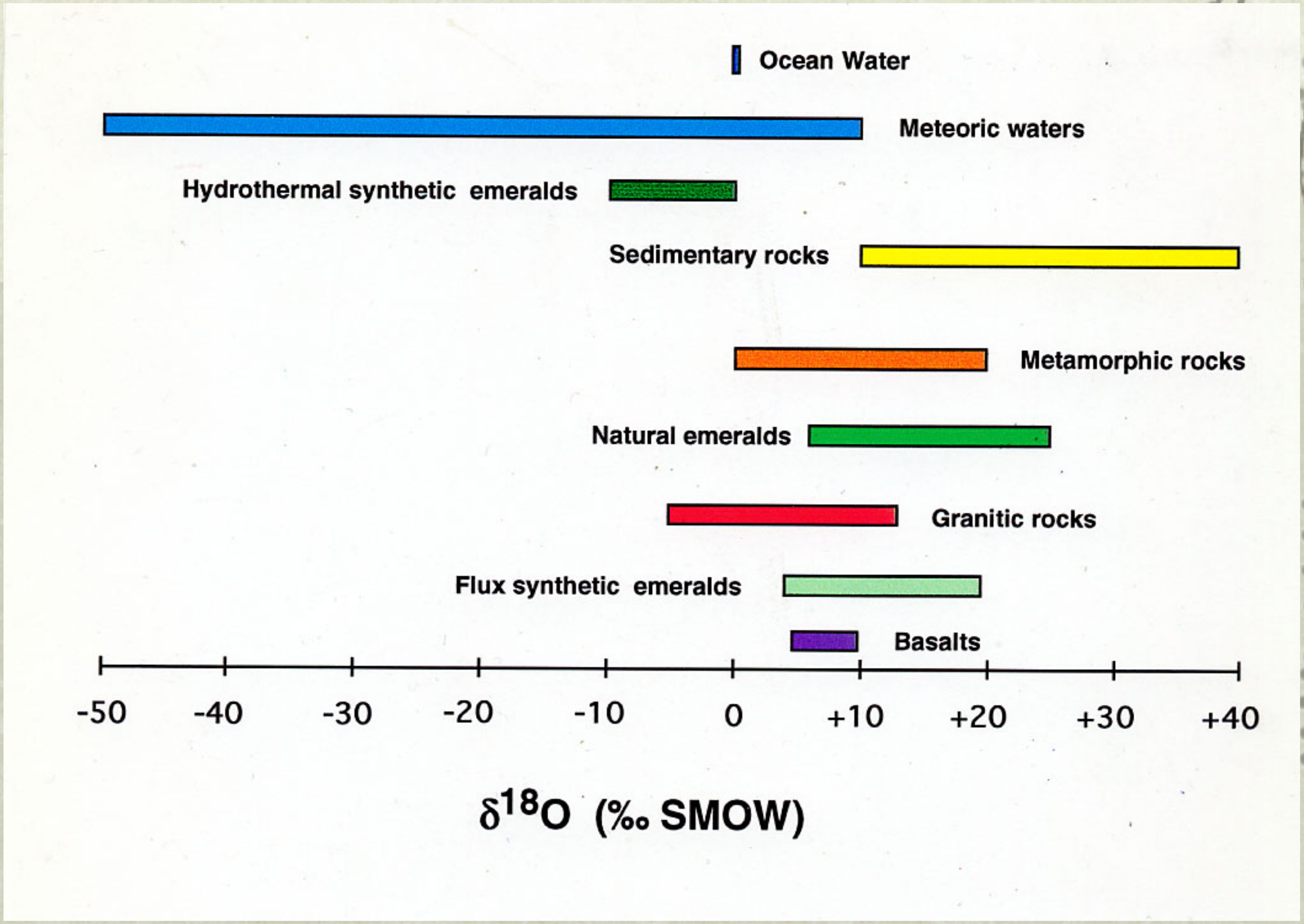
The $^{18}O/^{16}O$ ratio varies in relation with the geological context:

- source of oxygen
- temperature of crystallisation
- fluid-rock interaction

The variations of the $^{18}O/^{16}O$ ratio are in per mil following the notation $\delta^{18}O$ (‰, SMOW) with:

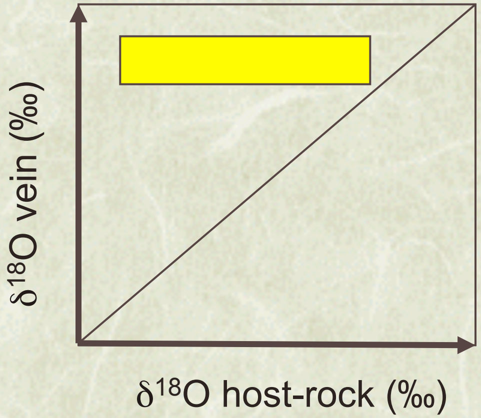
$$\delta^{18}O = (^{18}O/^{16}O_{sample} / ^{18}O/^{16}O_{standard} - 1) \times 1000$$

Natural oxygen isotopic ranges for geological material

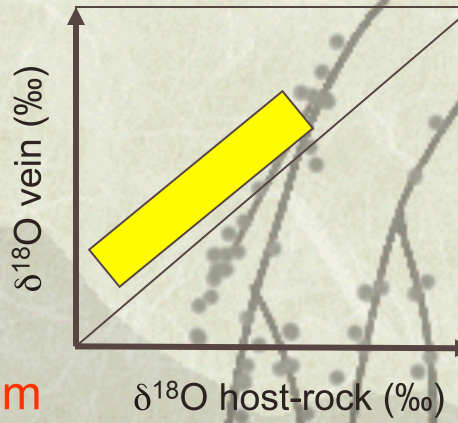


OXYGEN in EMERALD

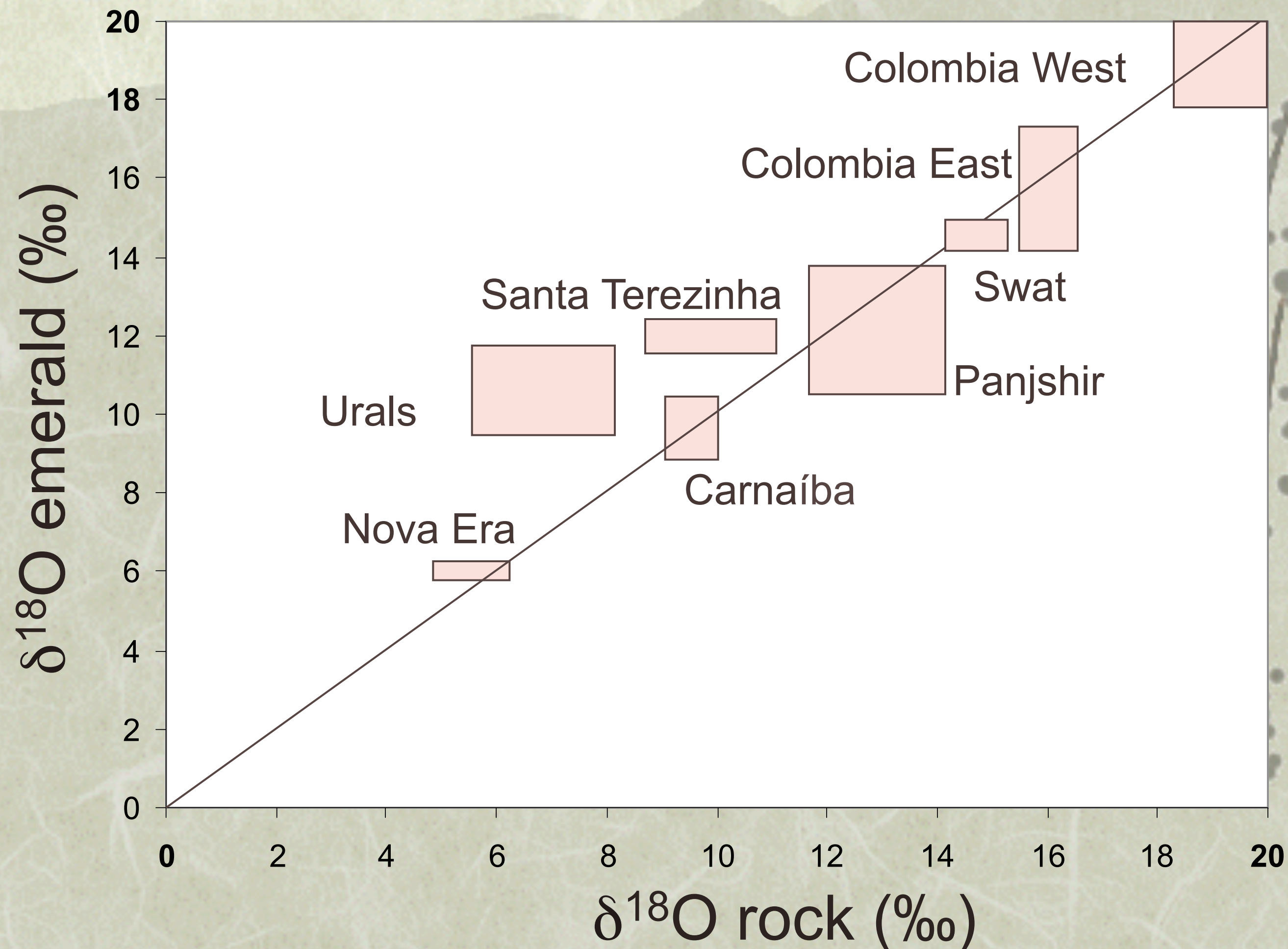
-Origin of the fluid
- Fluid-rock interaction
- (T, F/R → metasomatism)



Open system



Closed system




Mogok ruby

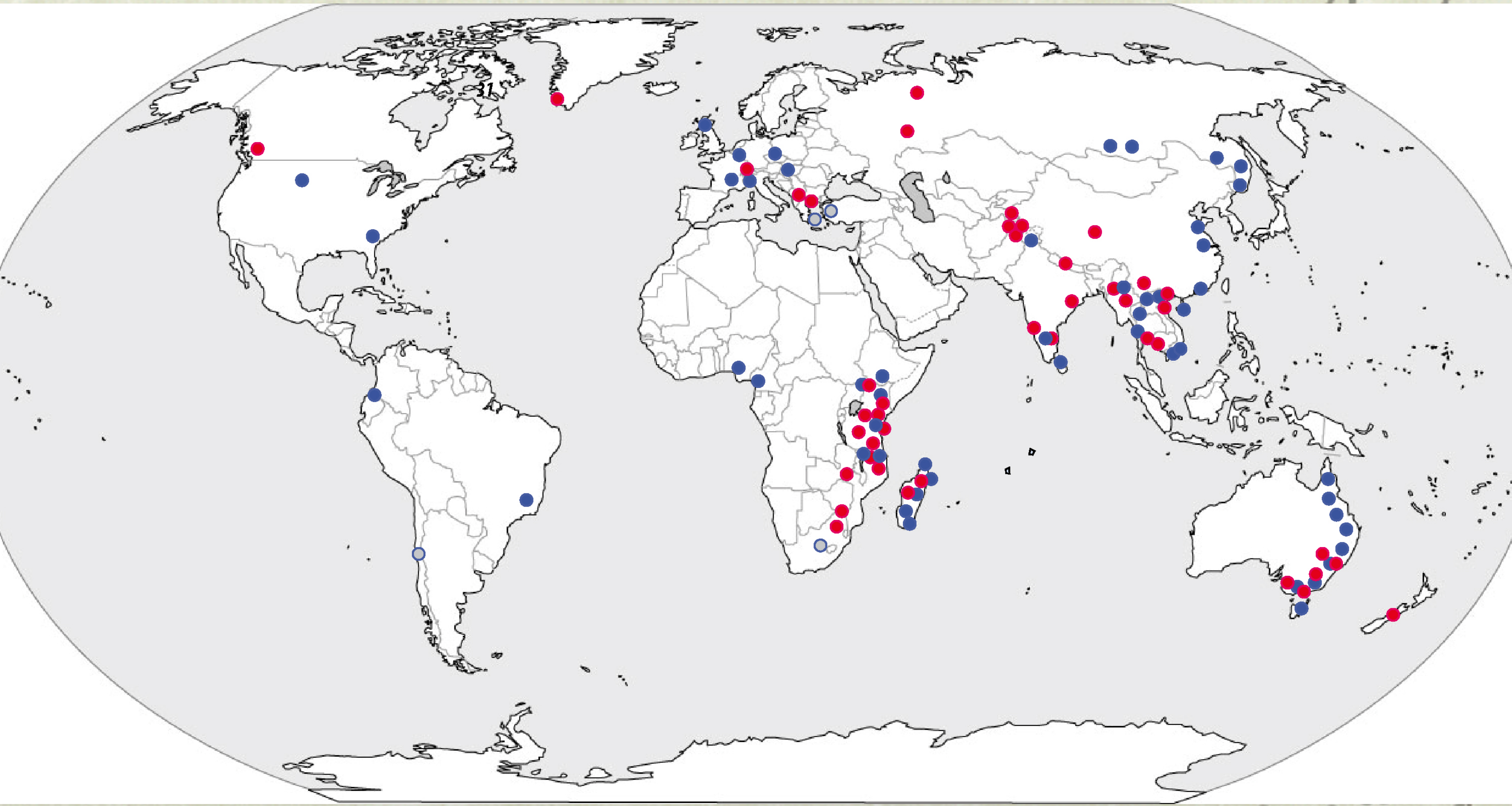

Montepuez ruby


Trapiche ruby

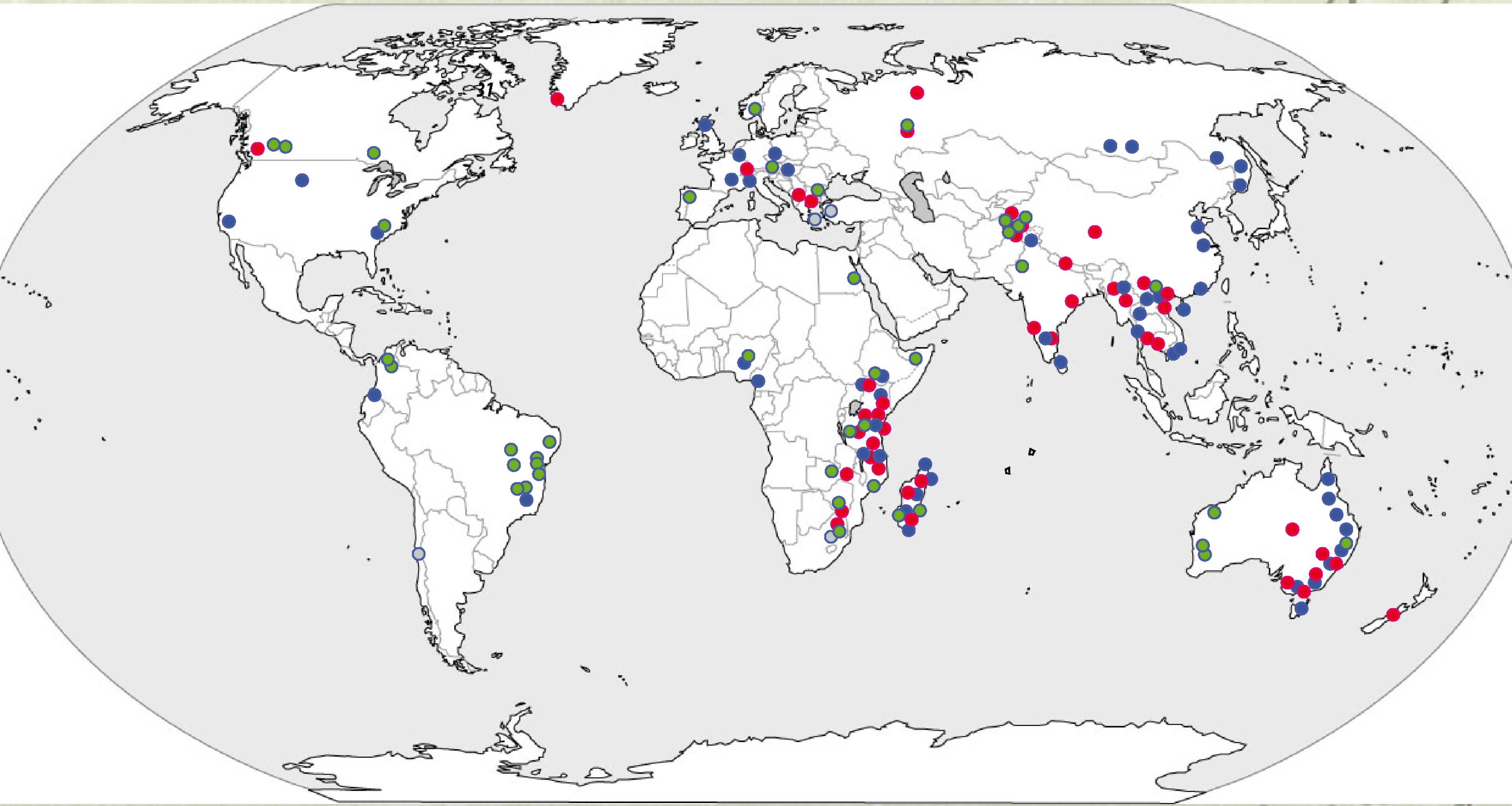
2

Age correlation of gems and tectono-magmatic events

Corundum deposits worldwide



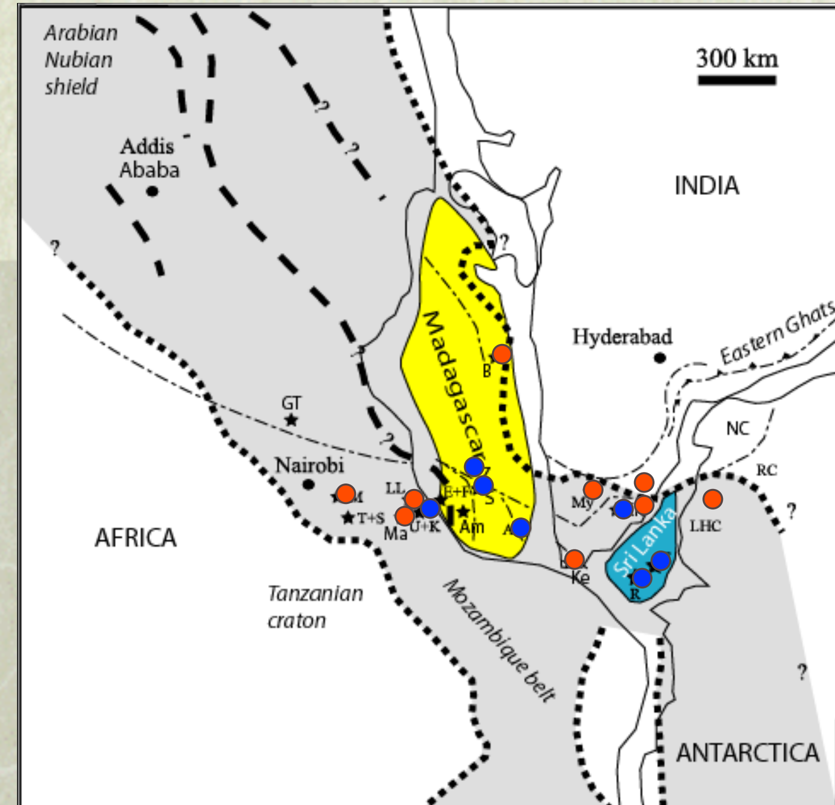
Corundum and emerald deposits worldwide



Ages of corundum deposits

The East African and Kuunga orogenesis (750-500 Ma)

The Neoproterozoic metamorphic mozambique corundum belt



Early Neoproterozoic rocks and/or region affected by the 750-500 Ma high grade metamorphism

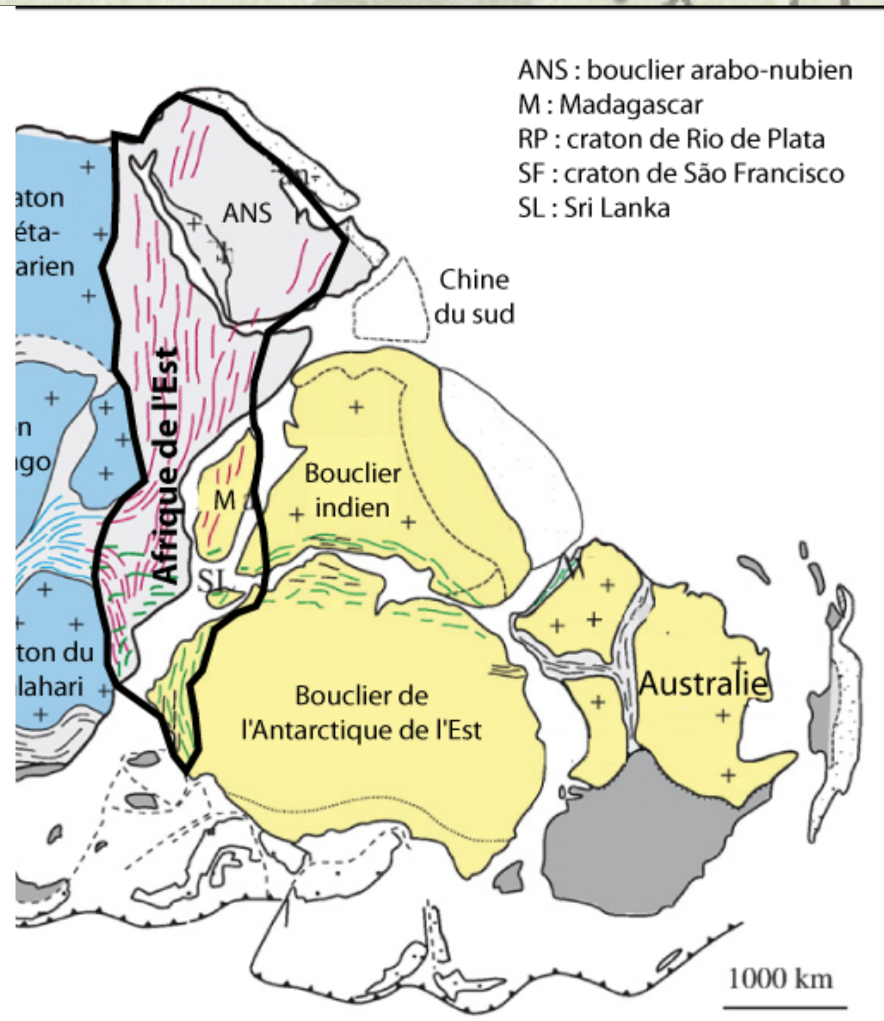
★ Primary corundum deposit

Neoproterozoic suture zone

Limit of Early Neoproterozoic rocks and/or region affected by the 750-500 Ma high grade deformation and metamorphism

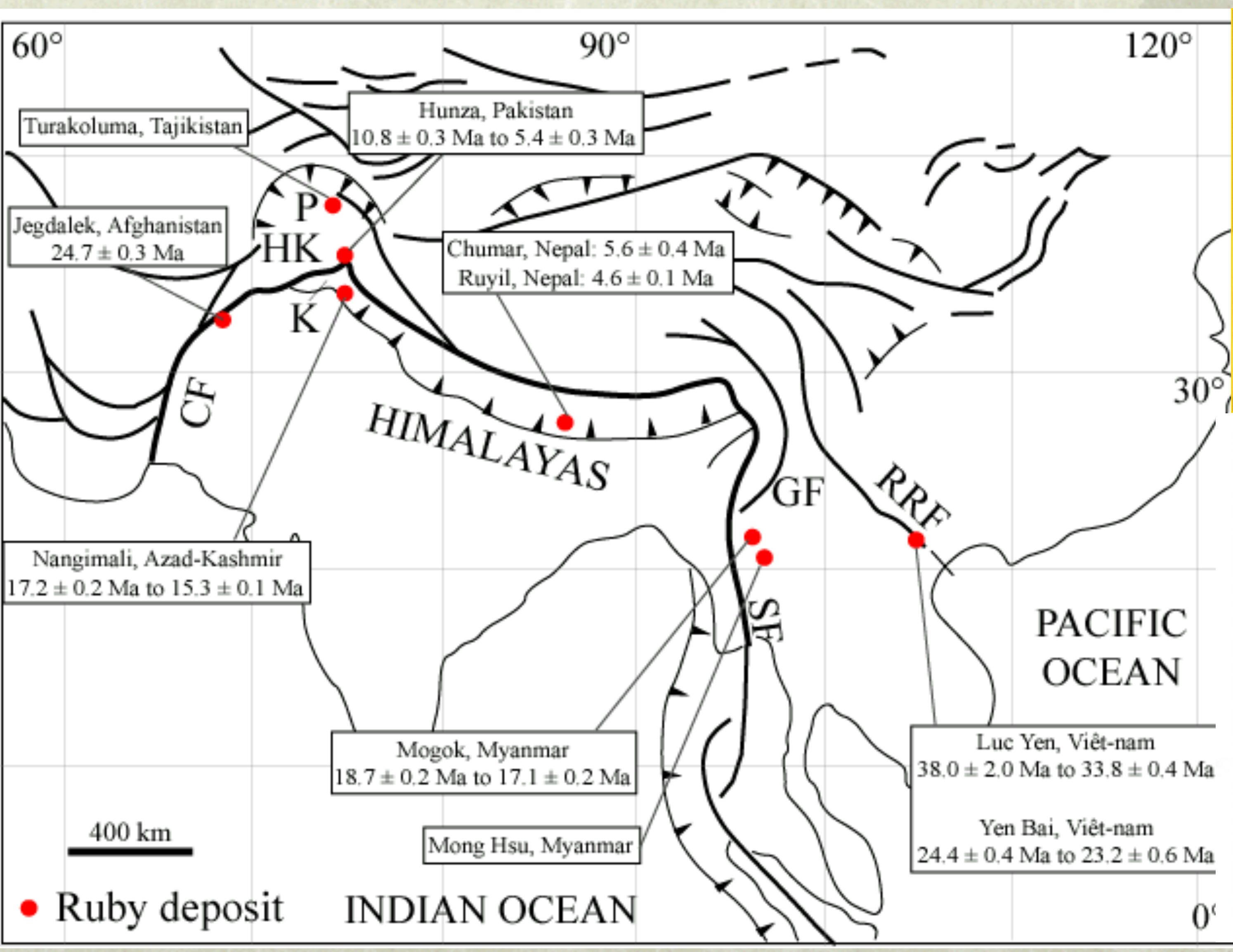
Thrust and shear zone

Garnier et al. (2004)



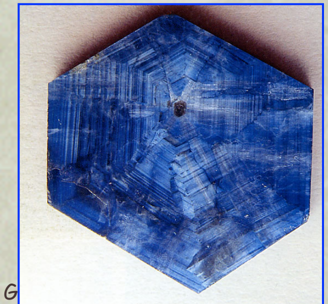
Ages of corundum deposits

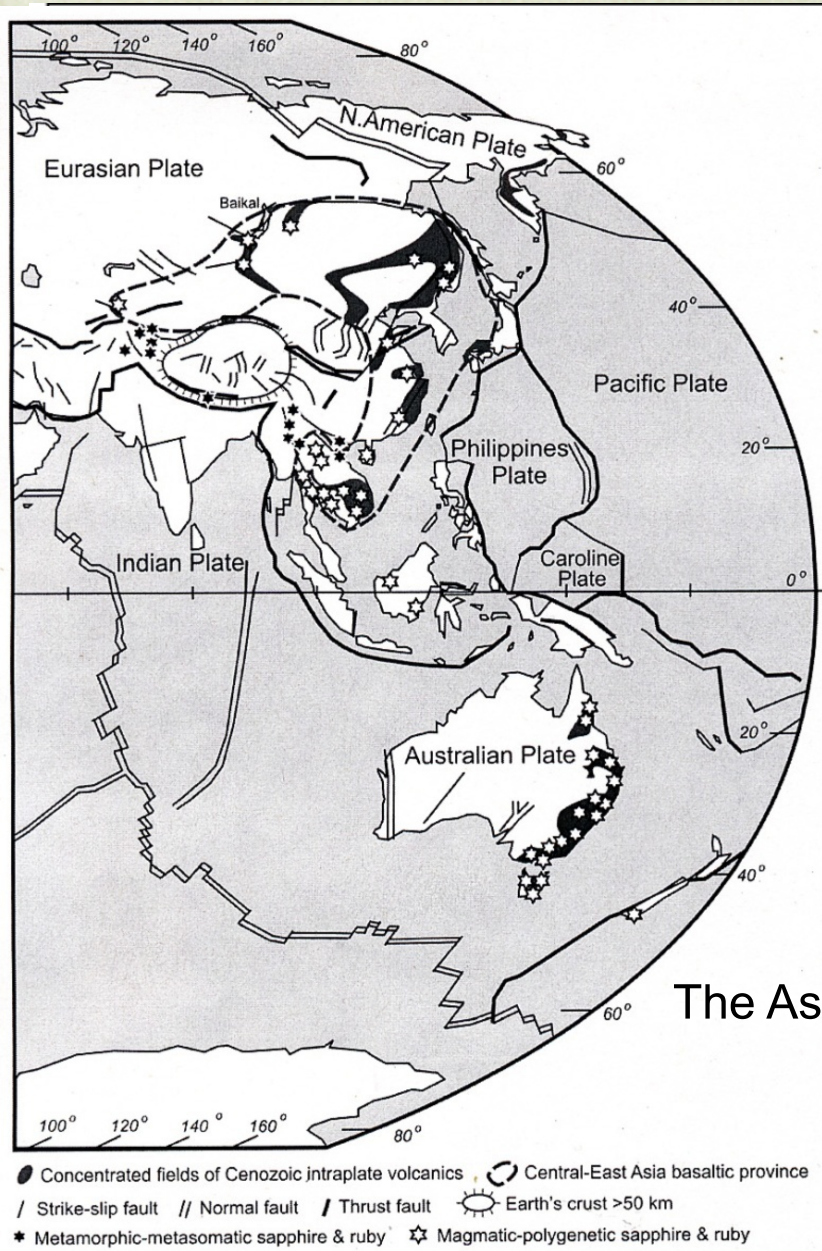
The Himalayan orogeny (45-5 Ma)

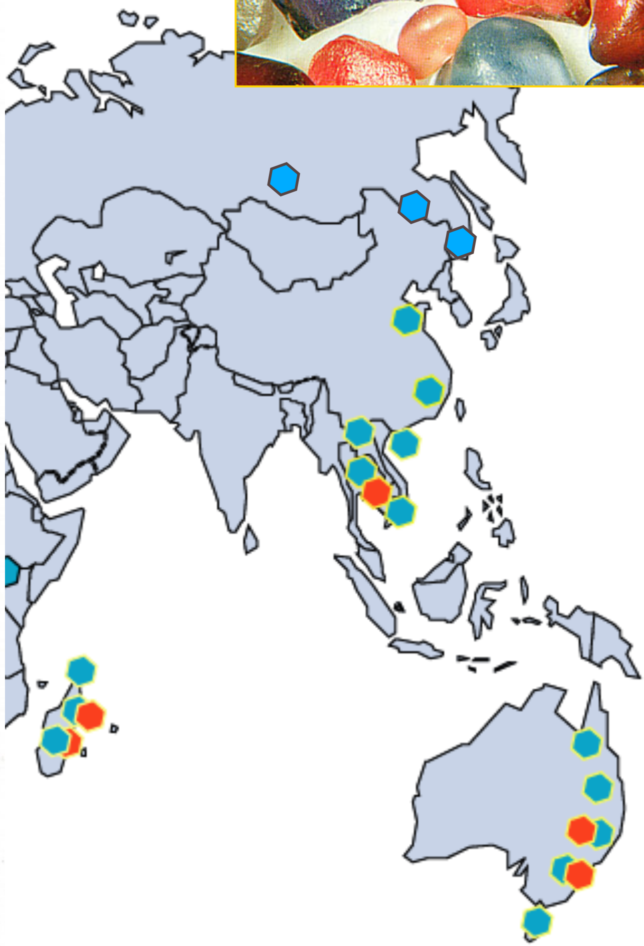


Ages of corundum deposits

The intraplate alkali basalts (65-1 Ma)







The Asian basaltic corundum province

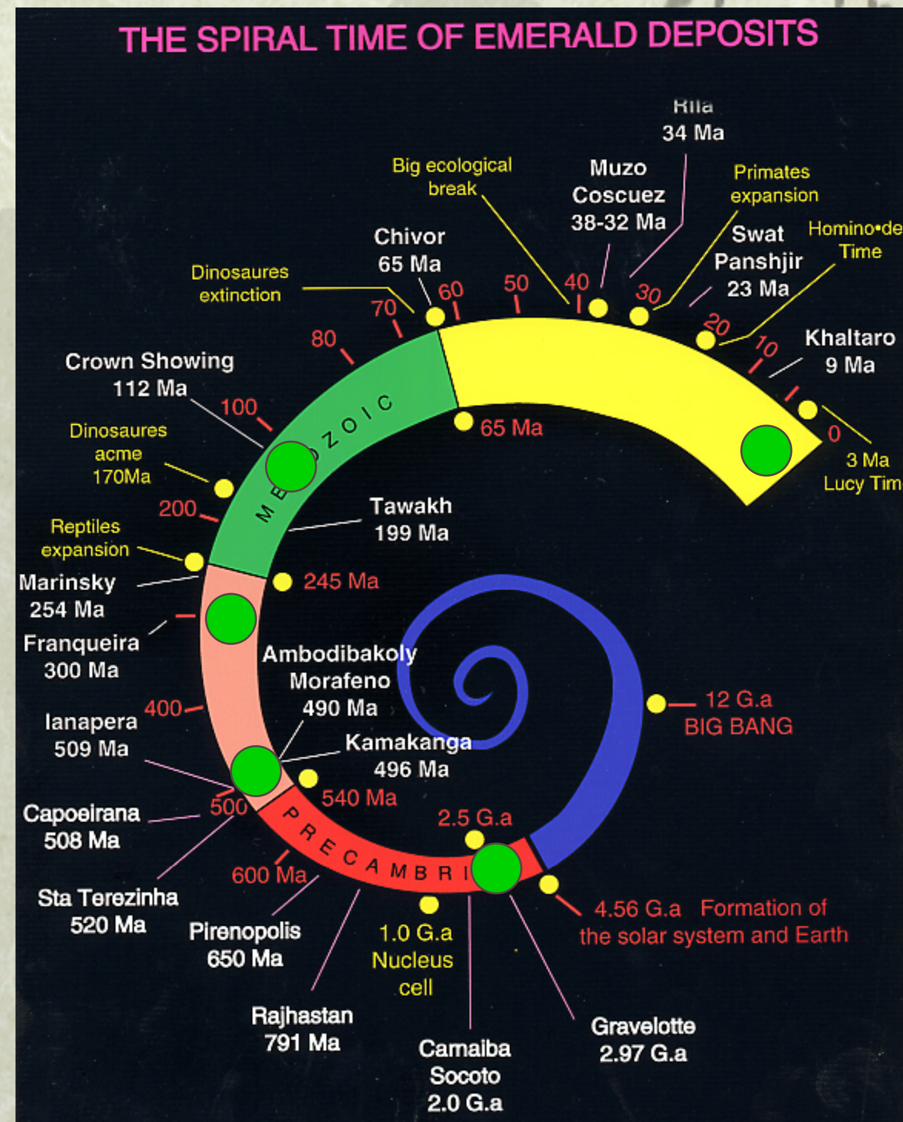
Thailand
Cambodia
China
Vietnam

Emerald deposits

Emerald: When ?


(extraLapis, 2002)


(extraLapis, 2002)



(Giuliani)

Continental collision domains (orogenesis):

¤ Eburnean -Transamazonian

¤ Pan-African-Brasiliano

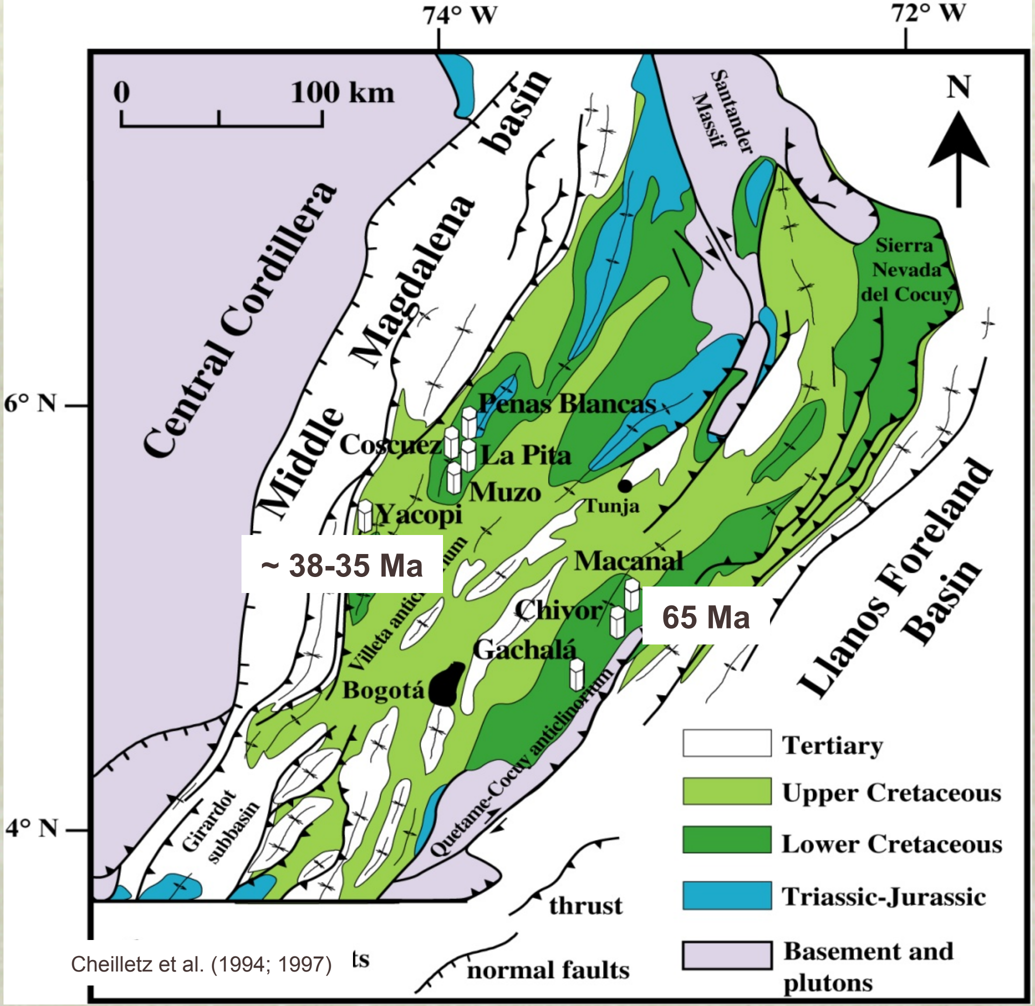
¤ Hercynian

¤ Yenshan

¤ Himalayan

and…. Colombian emeralds in the Eastern Cordillera ?

Two ages of formation (Eocene and lower Oligocene) and no magmatic activity:
The consequence of the acceleration of the convergence rate between the Nazca and South American plates.

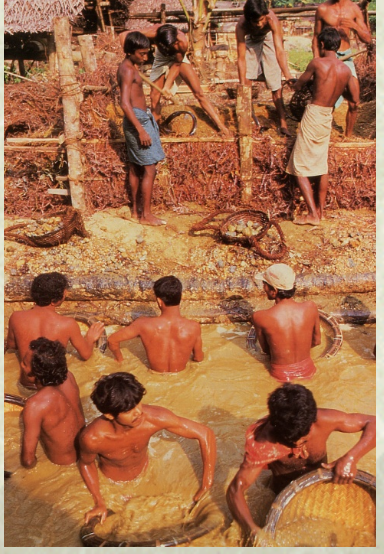


Cheilletz et al. (1994; 1997)

Muzo Giant, 1759 ct, 8.9 x 5 cm;
Schwarz (2002)

Deformation and structuring of the Eastern Cordillera basin:
Formation of the emerald deposits hosted in black shales.


Nangimali ruby deposit


Corundum in Sri Lanka


Coscuez emerald deposit

3

Genesis of the main economic types of corundum and emerald deposits

Main economic types of primary corundum and emerald deposits

I- METAMORPHIC DEPOSITS

Deposits hosted in marine sediments from carbonated platform

- ***Emerald in black shale***
- ***Ruby in marble***

II- MAGMATIC DEPOSITS

Type II-A

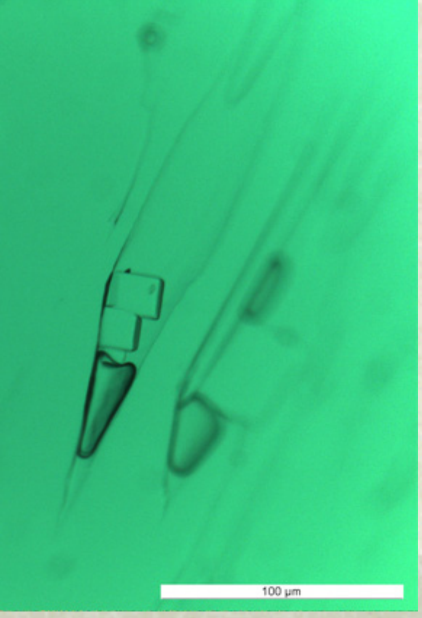
Deposits hosted in mafics-ultramafics and related to granitoidic intrusions and hydrothermalism

- ***Emerald in biotite schist and plagioclasite***
- ***Emerald in quartz, greisen-like veins pegmatite, aplite veins***
- ***Corundum in plagioclasite vein***

Type II-B

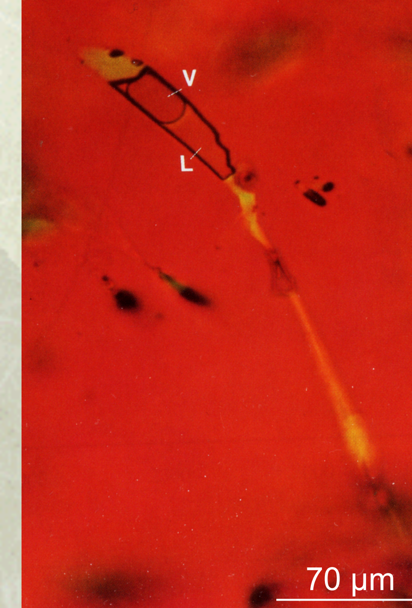
Deposits hosted in alkali basalts and mafic dykes

- ***Xenocrysts of corundum***
- ***Xenoliths of syenite with megacrysts of corundum***



Colombian fluid inclusion

Hunza valley ruby deposits



Fluid inclusion in ruby

3.1

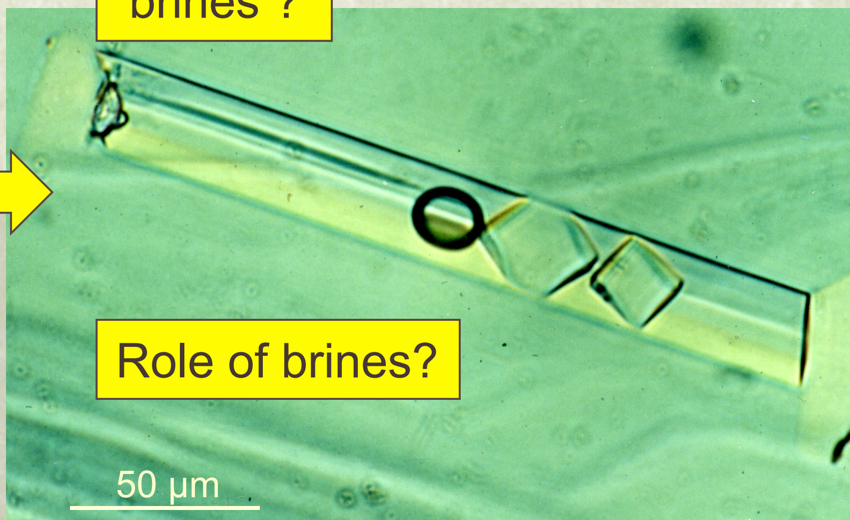
Deposits hosted in marine sediments from carbonated platform

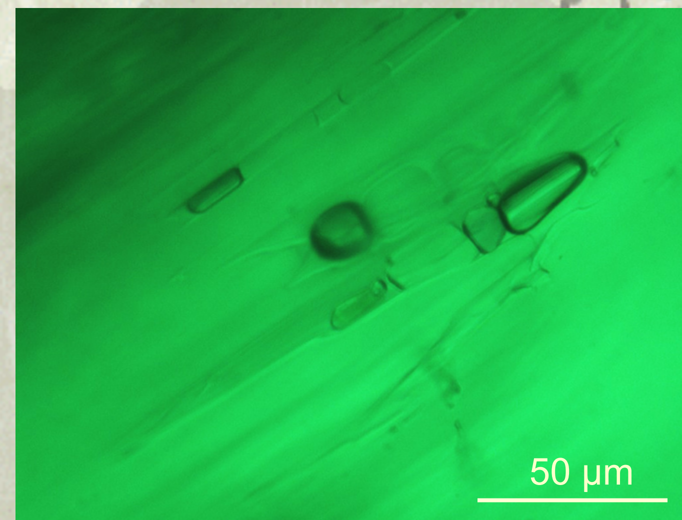
Fluids of evaporitic origin in ruby and emerald

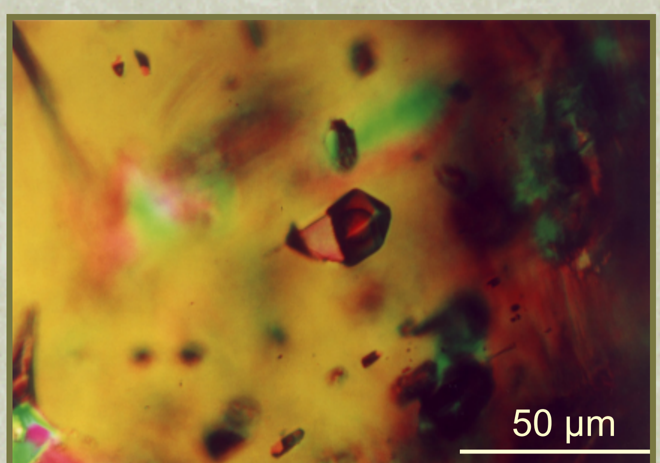
Brines, carbonic and sulfurous fluids, and molten salts

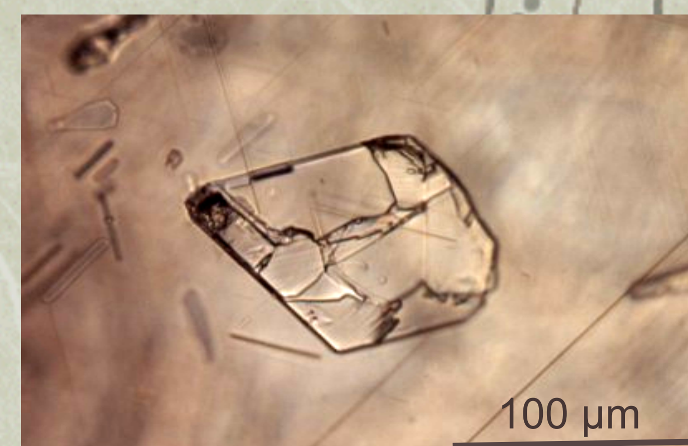
Emerald deposits (Colombia, Afghanistan, China)
Ruby deposits in marble (central and south-east Asia)

Origin of brines ?





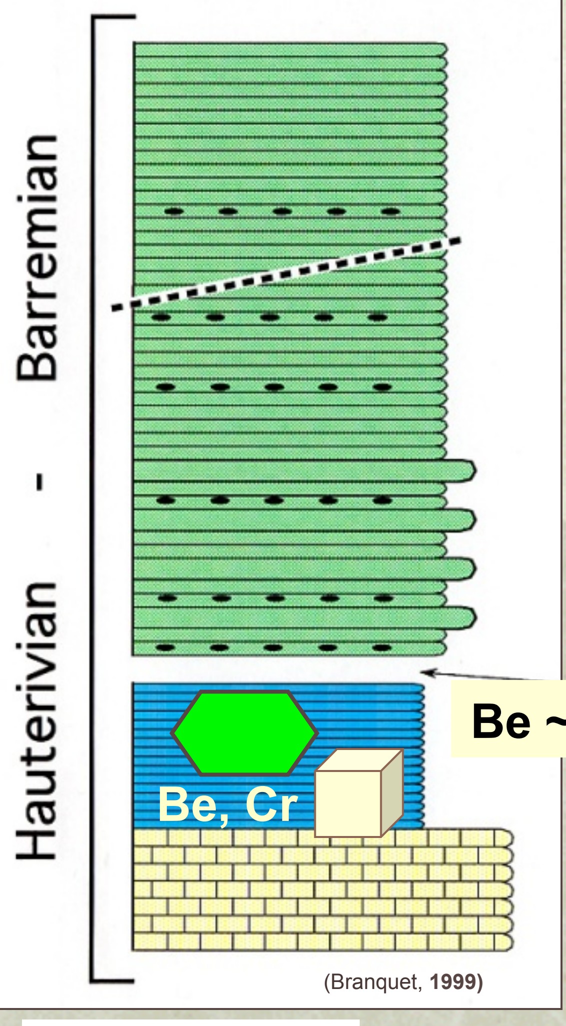




Metamorphic gems

Sedimentary basins

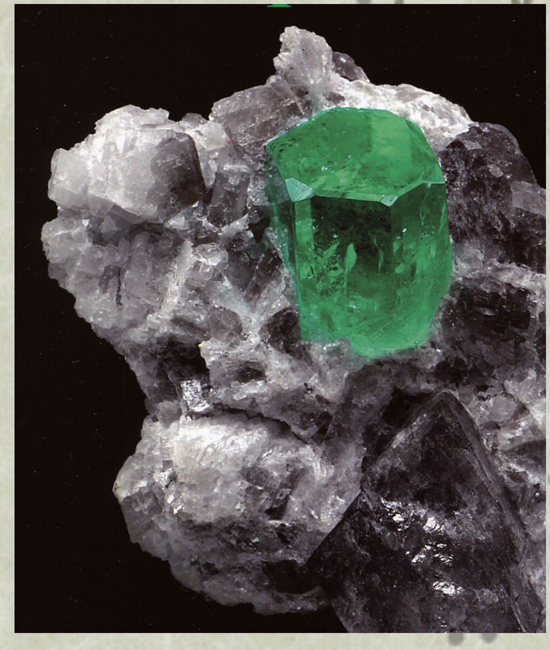
Black shales - carbonates - evaporites



Be ~4-5 ppm

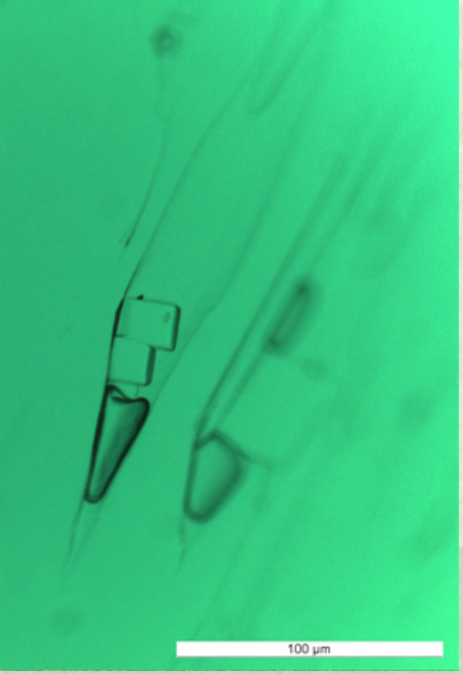
Age Em. ~ 65-35 Ma

Colombian emerald

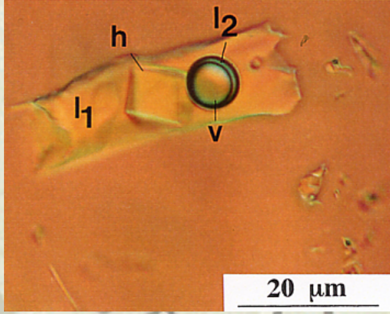


Andes

T = 300-330°C
depth = 7-9 km

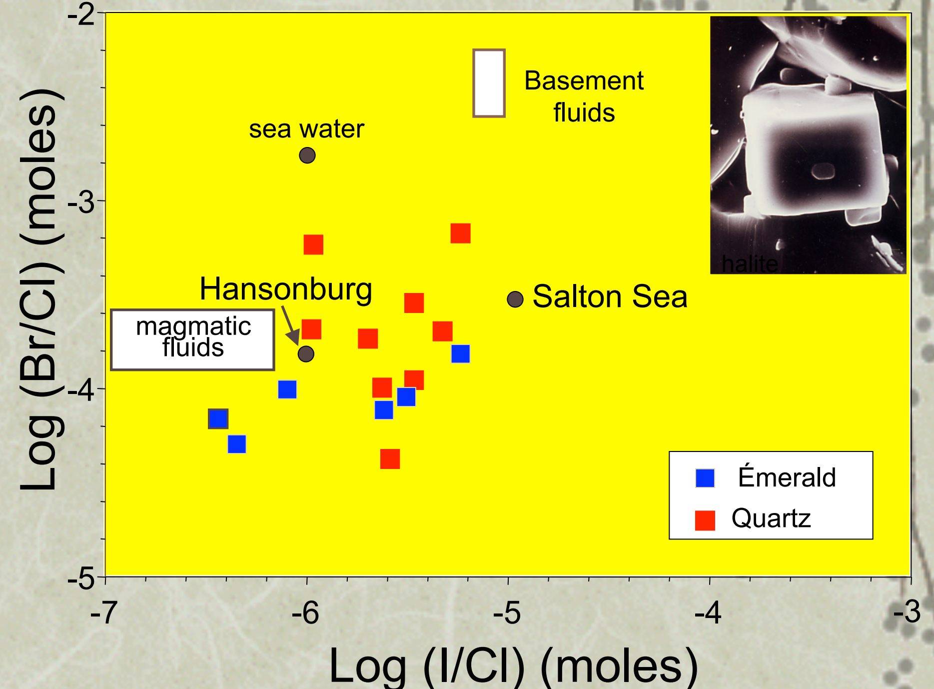


Characterization of the fluids



Highly saline fluids

H_2O-$NaCl$-CO_2-(Ca-K-Mg-Fe-Li-SO_4)
Salinity ~ 35-40 wt % eq. NaCl
« OPEN SYSTEM »



Colombian emerald

SO_4 ~ 400 - 500 ppm
Pb ~ 30 - 380 ppm
Zn ~ 200 - 300 ppm
Ba ~ 200 - 600 ppm
Li ~ 400 – 4300 ppm

Colombian emerald

O- and S- isotopes

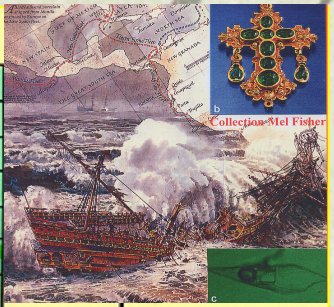
$16.2 < \delta^{18}O_{EmE} < 17.4‰$

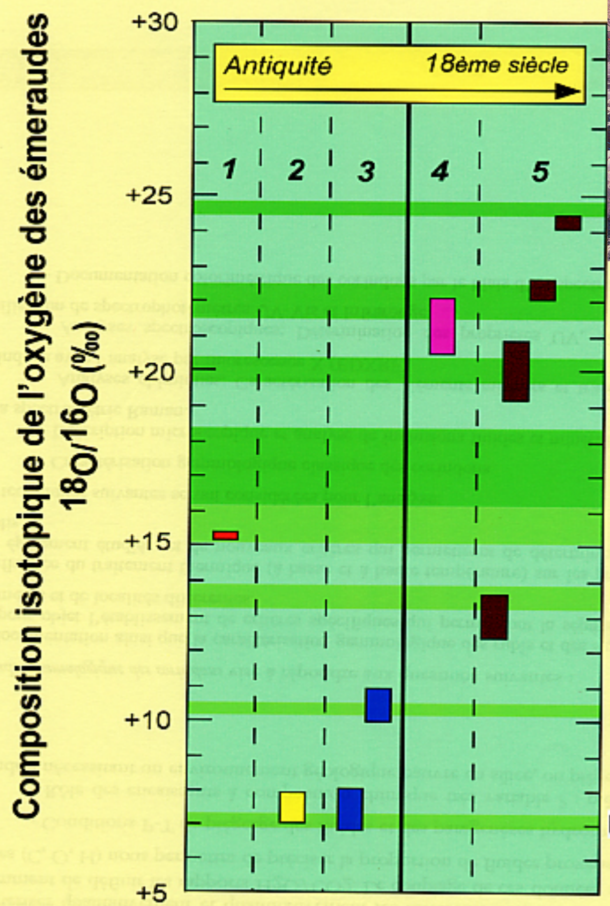
$18.7 < \delta^{18}O_{EmW} < 25.5‰$

$15.4 < \delta^{34}S_{Pyr} < 21.2‰$

$\delta^{18}O$ of emerald buffered by the $\delta^{18}O$ of the host-rocks

Mogul Emerald
Dated to 1695 • 217.80 carats





1 Boucle d'oreille Gallo-romaine (Méribel)

2 Emeraude du lys frontal de la Sainte Couronne de France

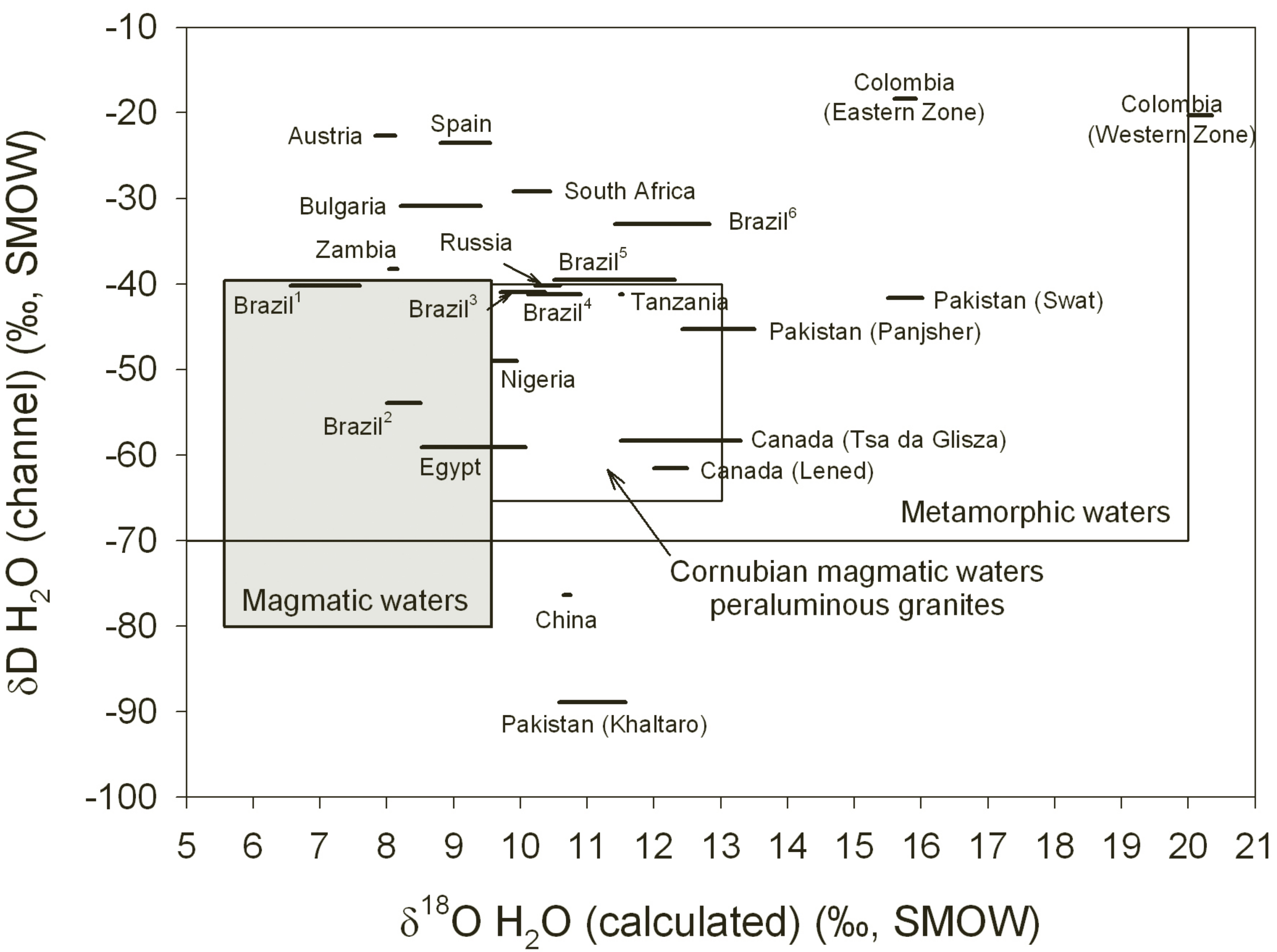
3 Emeraudes gemmes utilisées par l'Abbé Haüy

4 Emeraude du Galion espagnol 'Nuestra Senora de Atocha"

5 Emeraudes "Vieilles mines" (Trésor du Nizam d'Hyderabad"

Emeraudes historiques

(Giuliani et al., 2000)



Beryl-water oxygen fractionation equation (Taylor *et al.* (1992):

$$\mathbf{10^3\ ln\ a_{beryl-water\ (250-500\ °C)} = 1.579(106/\mathit{T}^2) - 0.645(10^3/\mathit{T}) - 2.522}$$

Role of the fluids in the genesis of emerald

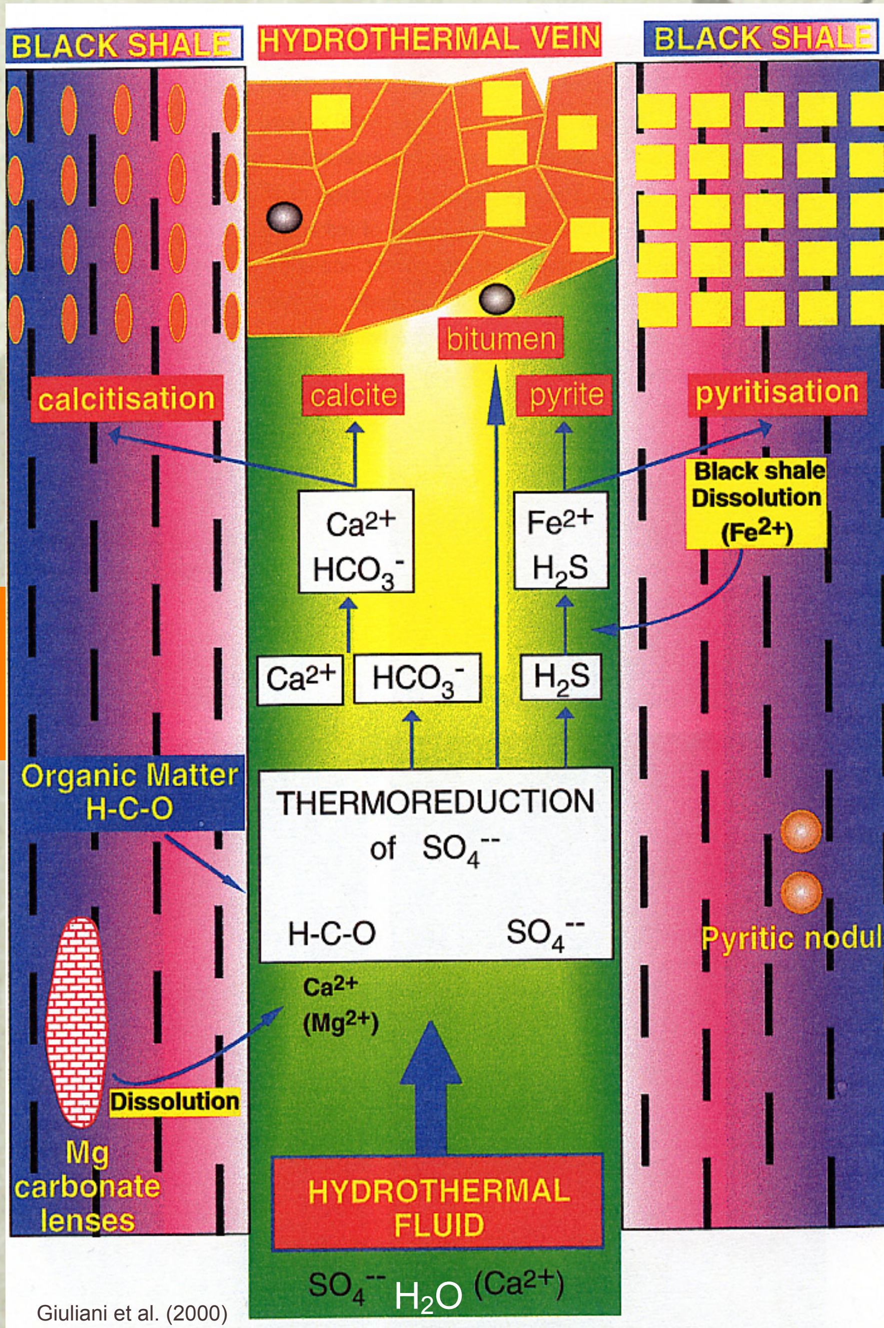
Thermal reduction of sulphates
à T ~ 300°C

Ra $(CH_2O)_2 + SO_4^{2-}$ (evaporitic origin)
$\rightarrow$
Rb (bitumen) + $2HCO_3^- + H_2S$

$HCO_3^- + Ca^{2+} \rightarrow CaCO_3$ (calcite) + H^+
and
$7H_2S + 4Fe^{2+} + SO_4^{2-} \rightarrow 4\,FeS_2$ (pyrite) + $4H_2O + 6H^+$

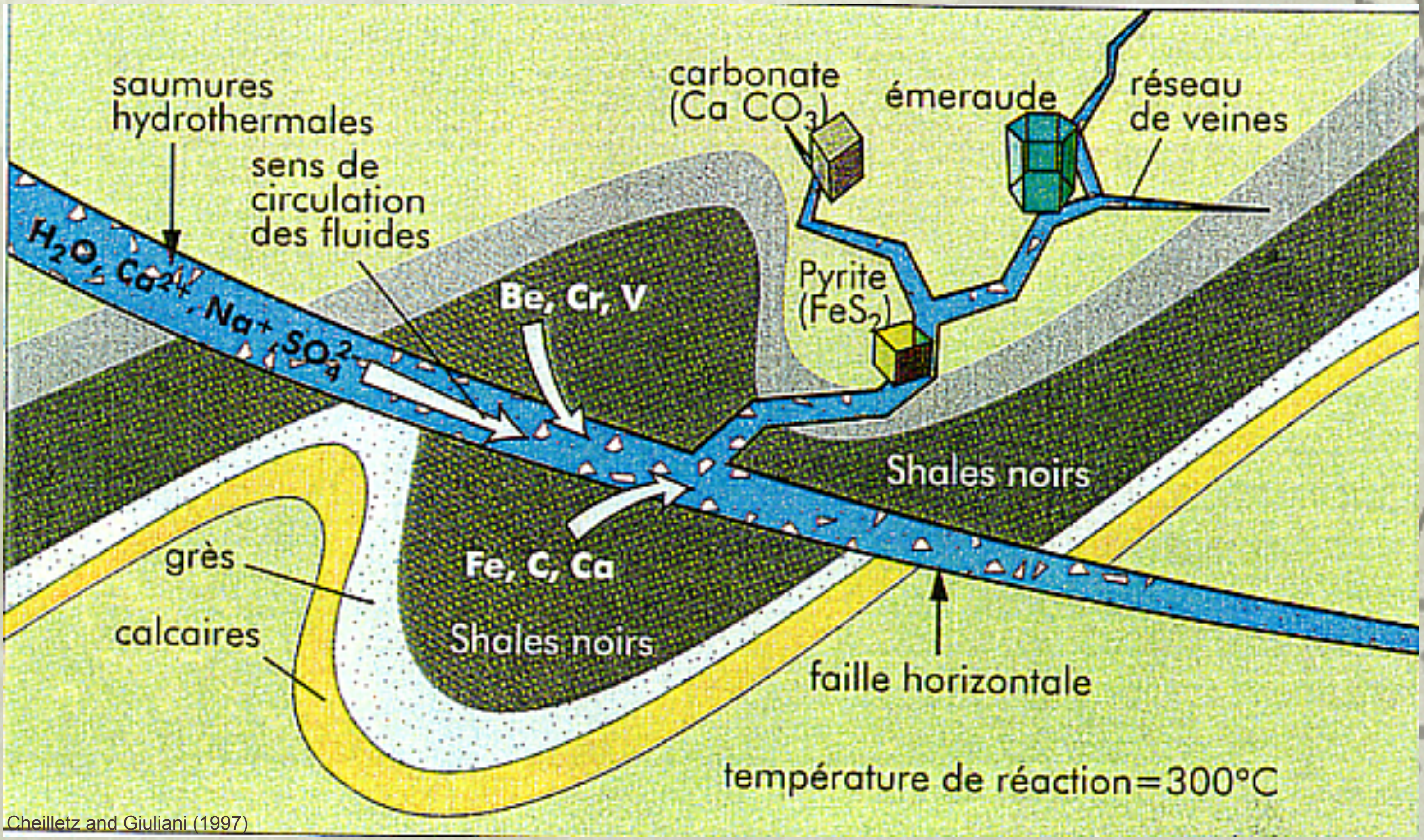
« OPEN SYSTEM »

Colombian emerald



Giuliani et al. (2000)

The model of formation of the Colombian emerald deposits

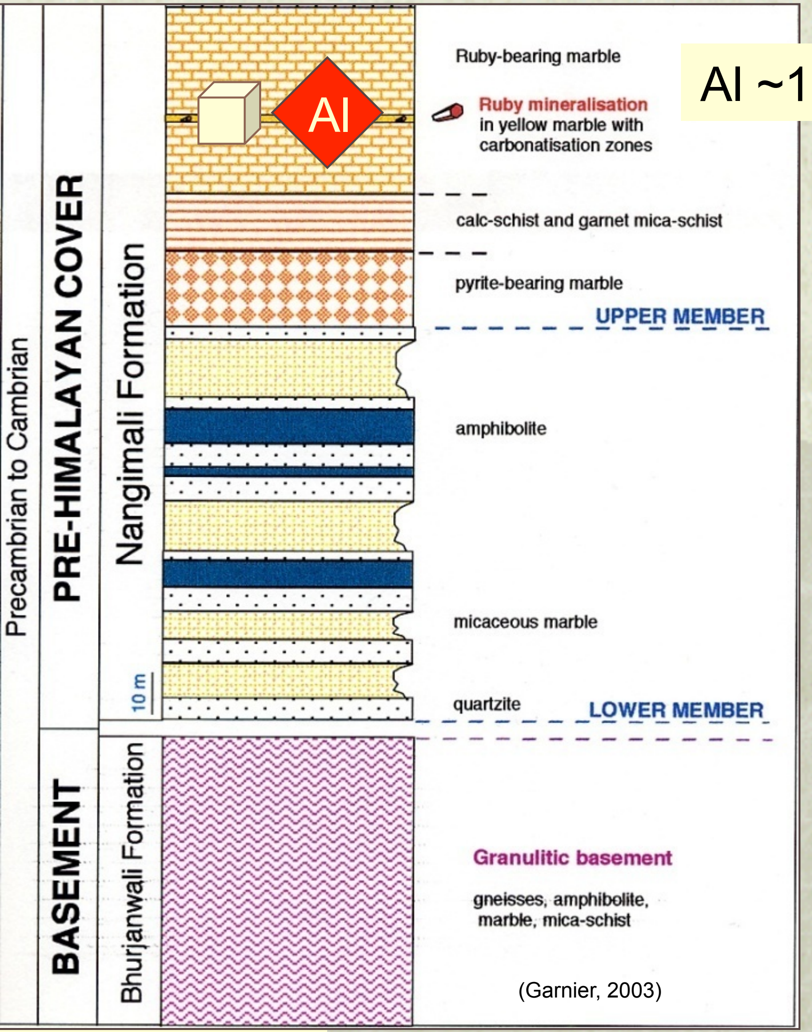


Cheilletz and Giuliani (1997)

Metamorphic gems

Sedimentary basins

Black shales - carbonates - evaporites



Al ~1000 ppm

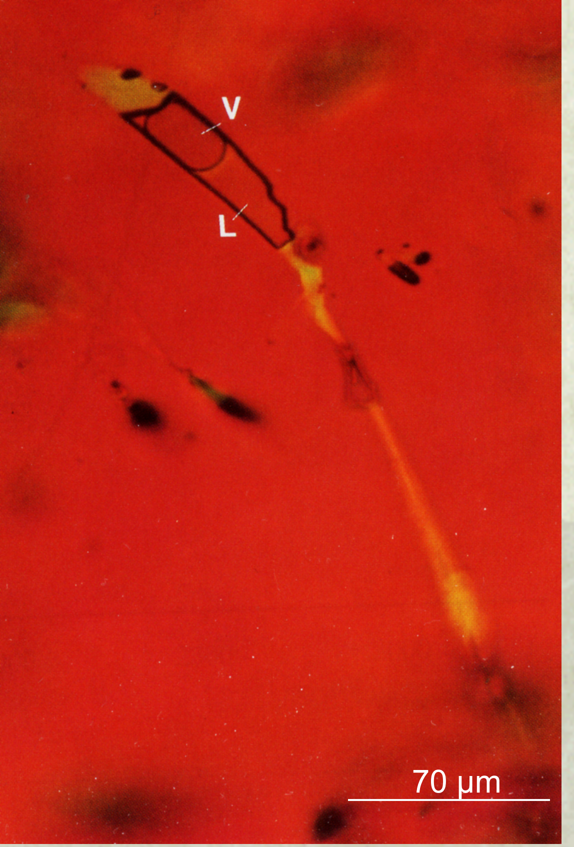
Age rubis ~ 38-5 Ma

Himalayas

T= 620-670°C
depth = 21-22 km

Ruby in marble from
central and south-east Asia

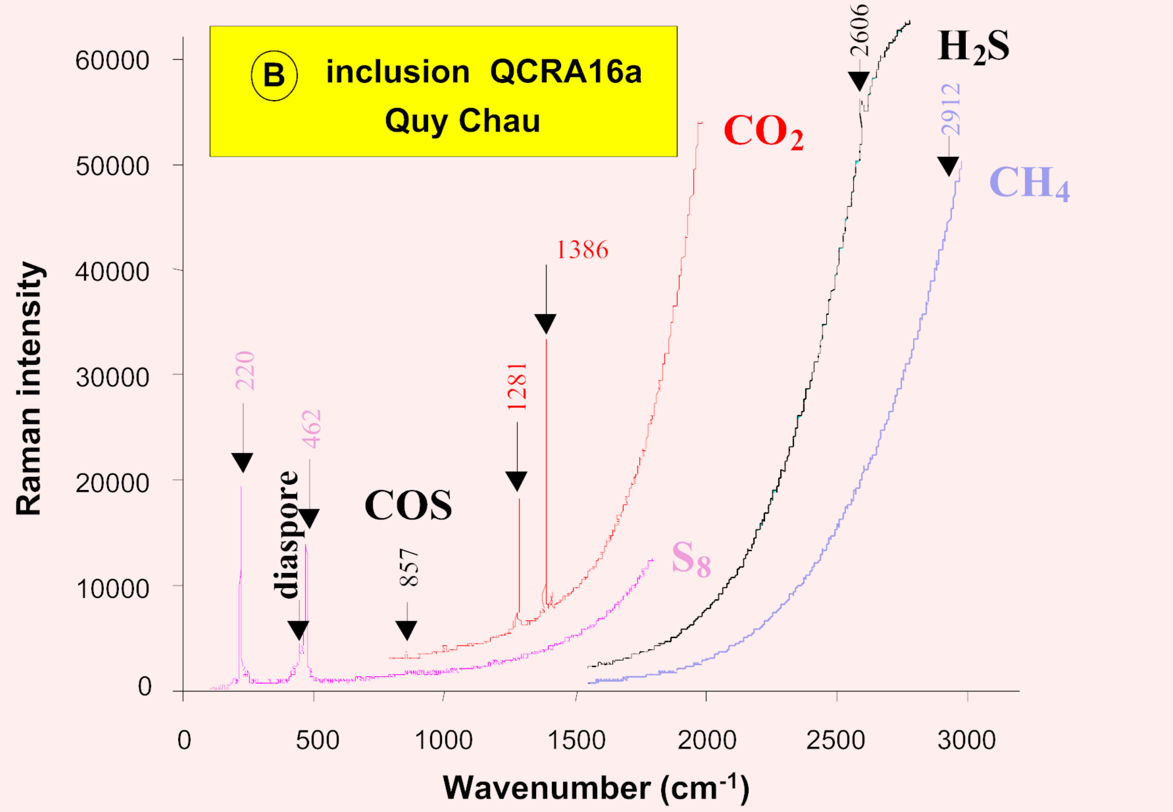
Characterization of the fluids



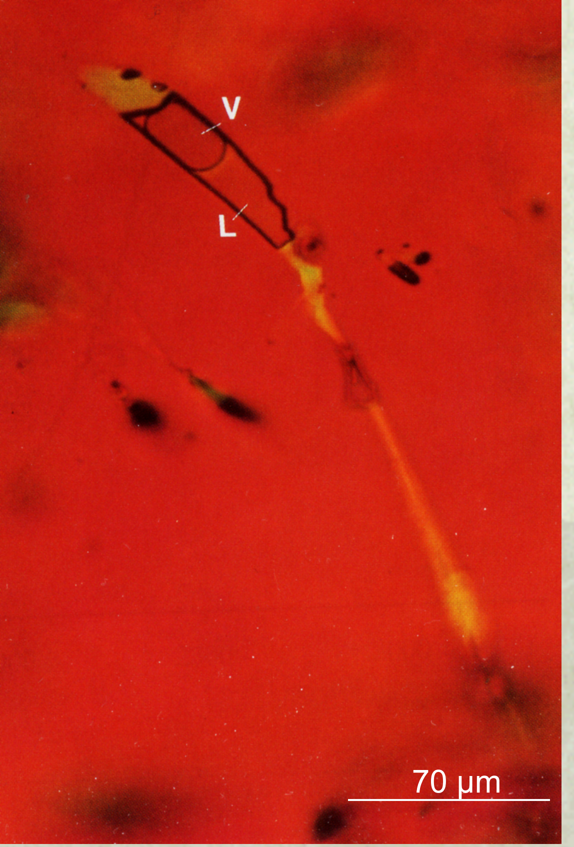
Constituents of the fluids

CO_2-H_2S-COS-S_8-AlO(OH)

« CLOSED SYSTEM »



Ruby
in marble



Characterization of the fluids

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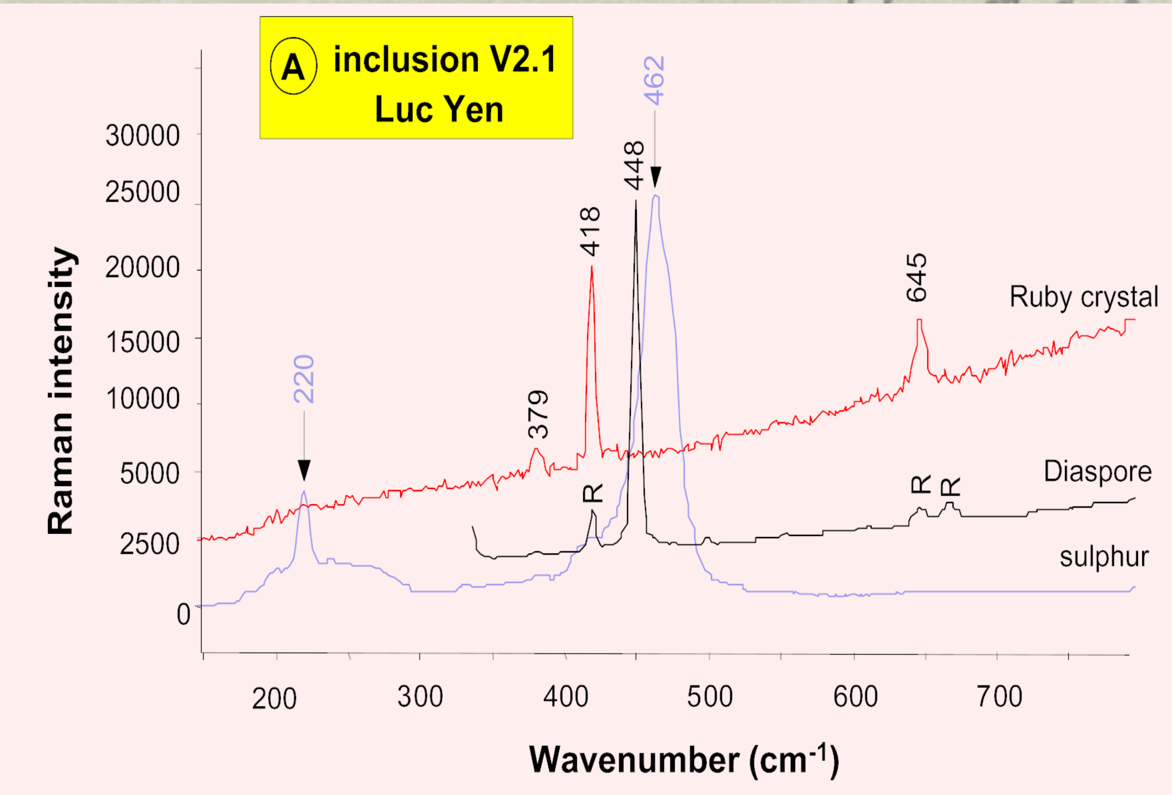
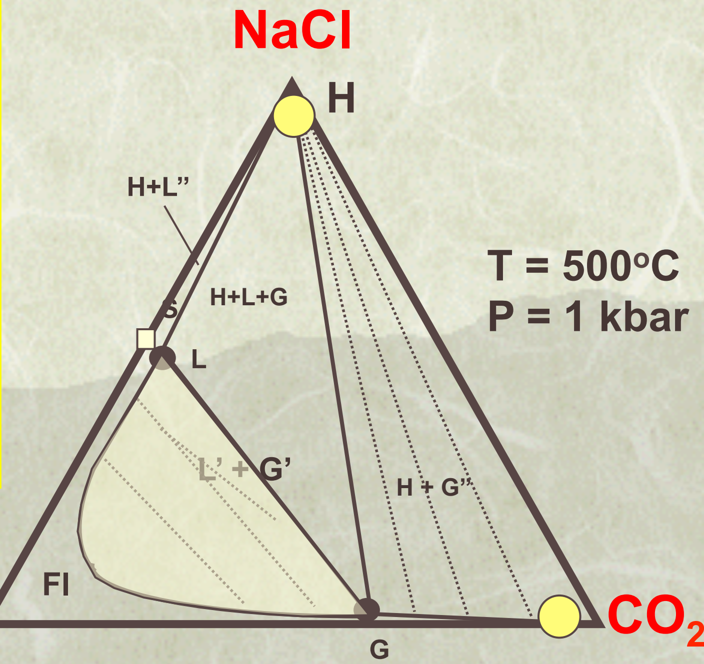
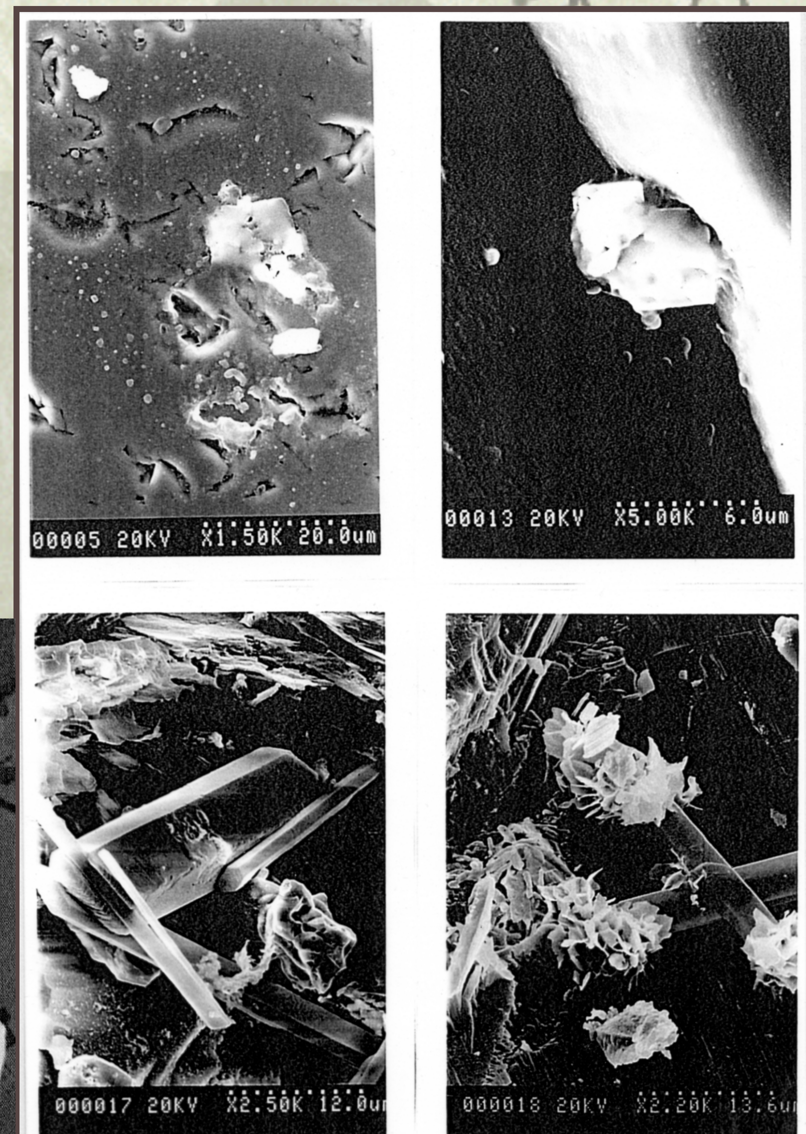


Ruby
in marble

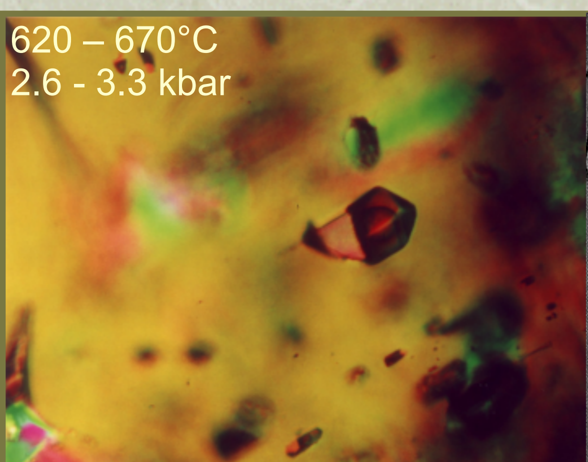
Evaporitic origin of the salts and sulphates

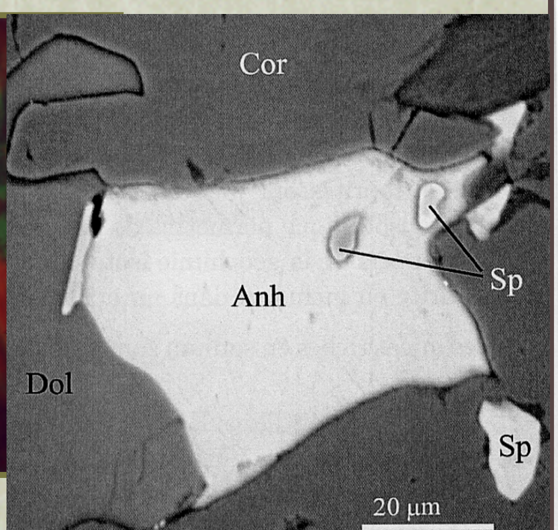


Fluid inclusions:
CO_2-H_2S-COS-S_8-AlO(OH) and salts



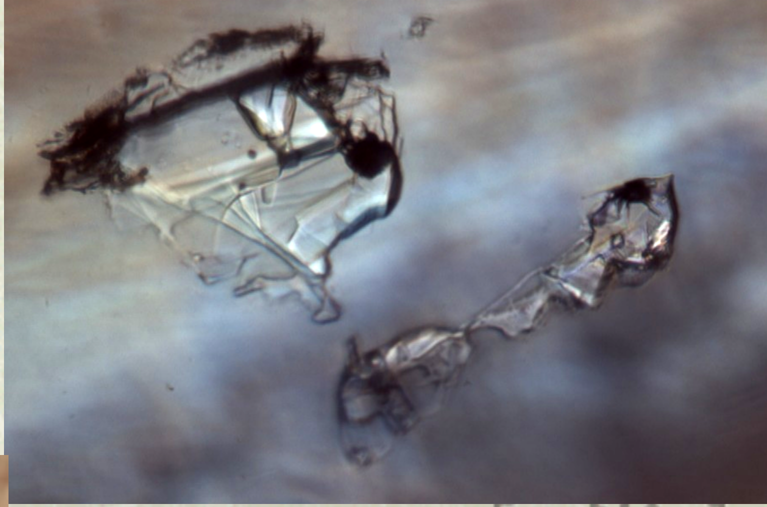
Giuliani et al. (2003)

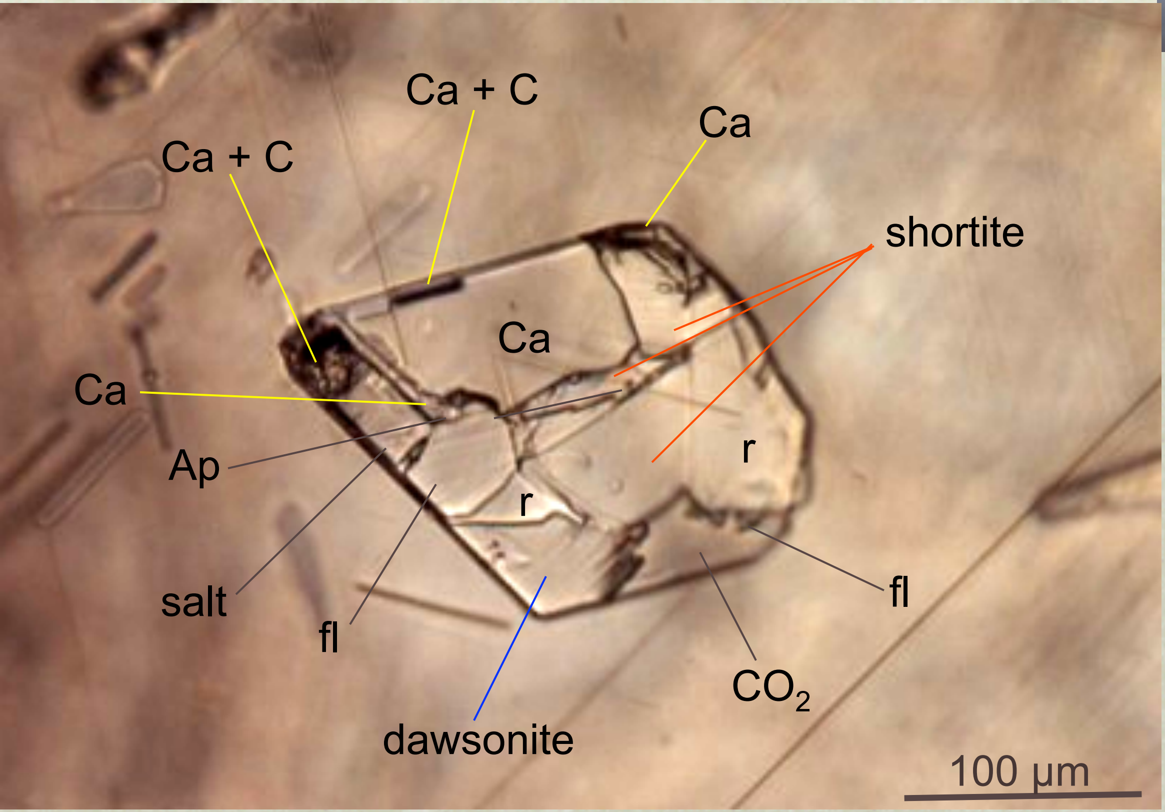




Garnier et al. (2008)

Characterization of the fluids





Molten salts
($Na-Ca-K-SO_4-CO_3$)

dawsonite ($NaAl(CO_3)(OH)_2$

shortite ($Na-Ca-CO_3$)

barite & sulfates (980 cm^{-1})

nitrates (1045, 1049, 1058 cm^{-1}),

and complex carbonates
(REE-carbonate ?)

and boehmite, graphite, rutile, fluorite,
calcite, dolomite, apatite…

and CO_2-H_2S-… and sometimes salts

Characterization of the fluids

Cations and anions
in the Flinc: Crushing

Mines	Minéral	Na	K	Li	F	Cl	Br	NO_3	SO_4
Khoan Thong	spinelle	**238**	161	5.8	192	**876**	4.3	**494**	**763**
Khoan Thong	**rubis**	**99**	70	0.7	126	**371**	1.9	**455**	**118**
Luc Yen	**rubis**	**251**	137	2.5	30	**784**	3.3	**379**	**1778**
An Phu	**rubis**	**132**	40	0.9	nd	**779**	3.3	**663**	**229**
Bai Dà Lan	**rubis**	**223**	193	1.1	nd	**651**	3.3	**309**	**106**
Quy Chau (Doi San)	spinelle	**375**	160	1.8	nd	**1576**	11.2	**396**	**553**

(en ppb)

Characterization of the fluids

Cations and anions
in the Flinc: Crushing

Na^+, Cl^- et SO_4^{2-} ➡ Presence of minerals of evaporitic origin: salts and sulphates

NO_3^- ➡ Evaporitic lakes of continental origin ?

Ruby in marble

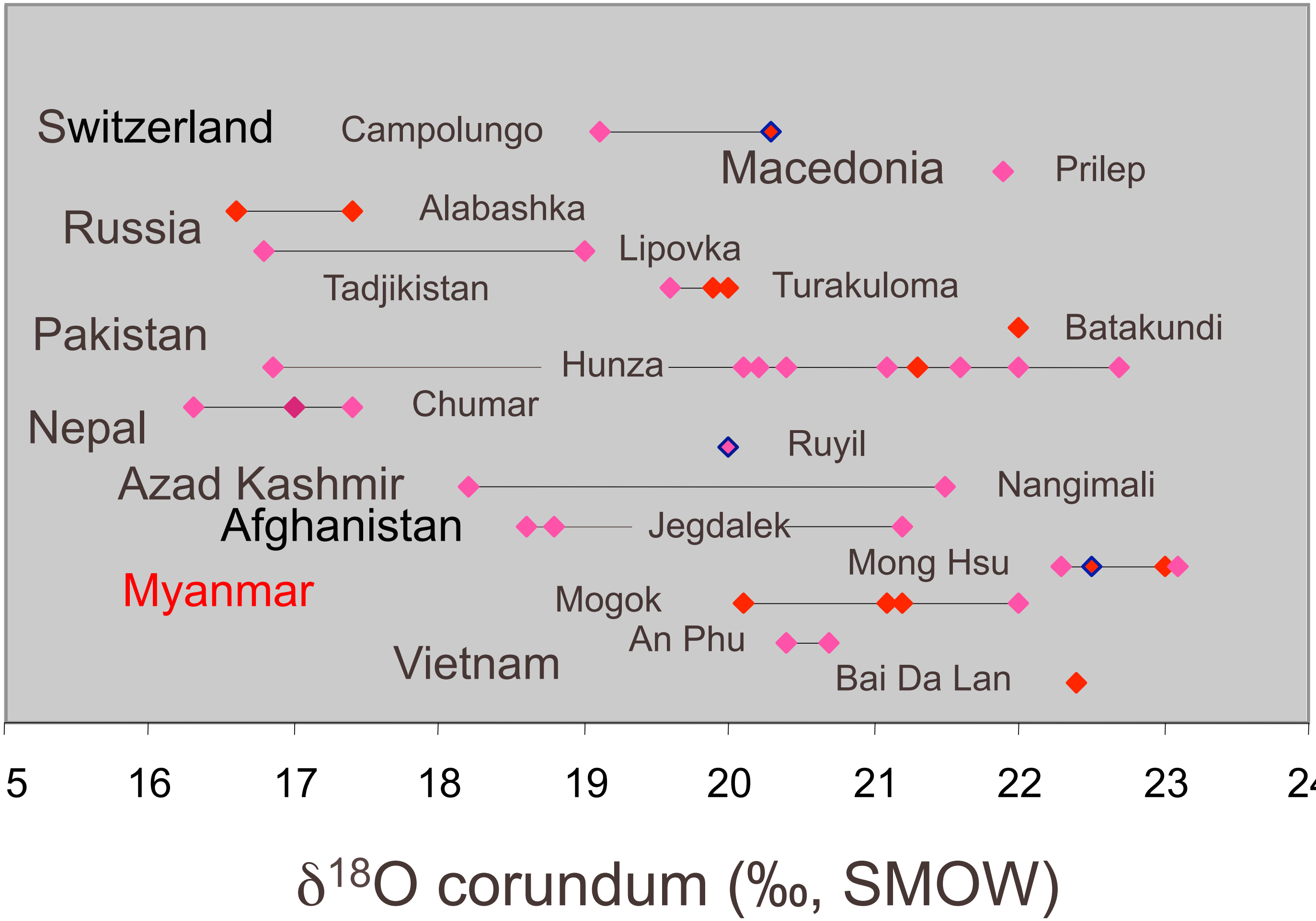
$16.5 < \delta^{18}O_{Rub} < 23.2‰$

$1.6 < \delta^{34}S_{Anhy} < 4.8‰$

$23.3 < \delta^{34}S_{Anhy} < 27.4‰$

$-10,5 < \delta^{11}B_{Tour} < -0,4\ ‰$

O- S- and B- isotopes



Role of the fluids in the genesis of ruby

Thermal reduction of sulphates
à T ~ 600-650°C

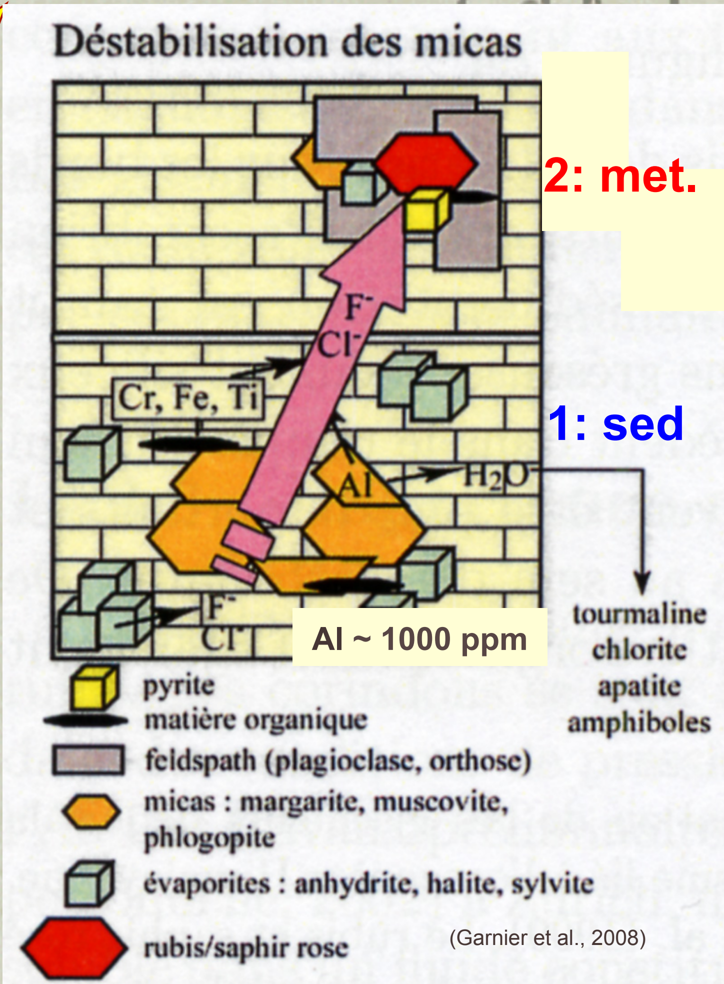
Association
carbonate-graphite-evaporites

$2CaSO_4$ (anhydrite) + 3C (graphite) → $2S^{\circ}$ (fluid) + $2CaCO_3$ (calcite) + CO_2 (fluid)
$CaSO_4 + C + H_2O \rightarrow H_2S + CaCO_3 + CO_2$

$Fe^{2+} + H_2S \rightarrow 2H^+ + FeS_2$
(pyrite)

« CLOSED SYSTEM »

Ruby in marble



(Garnier et al., 2008)

Zambian emerald in quartz

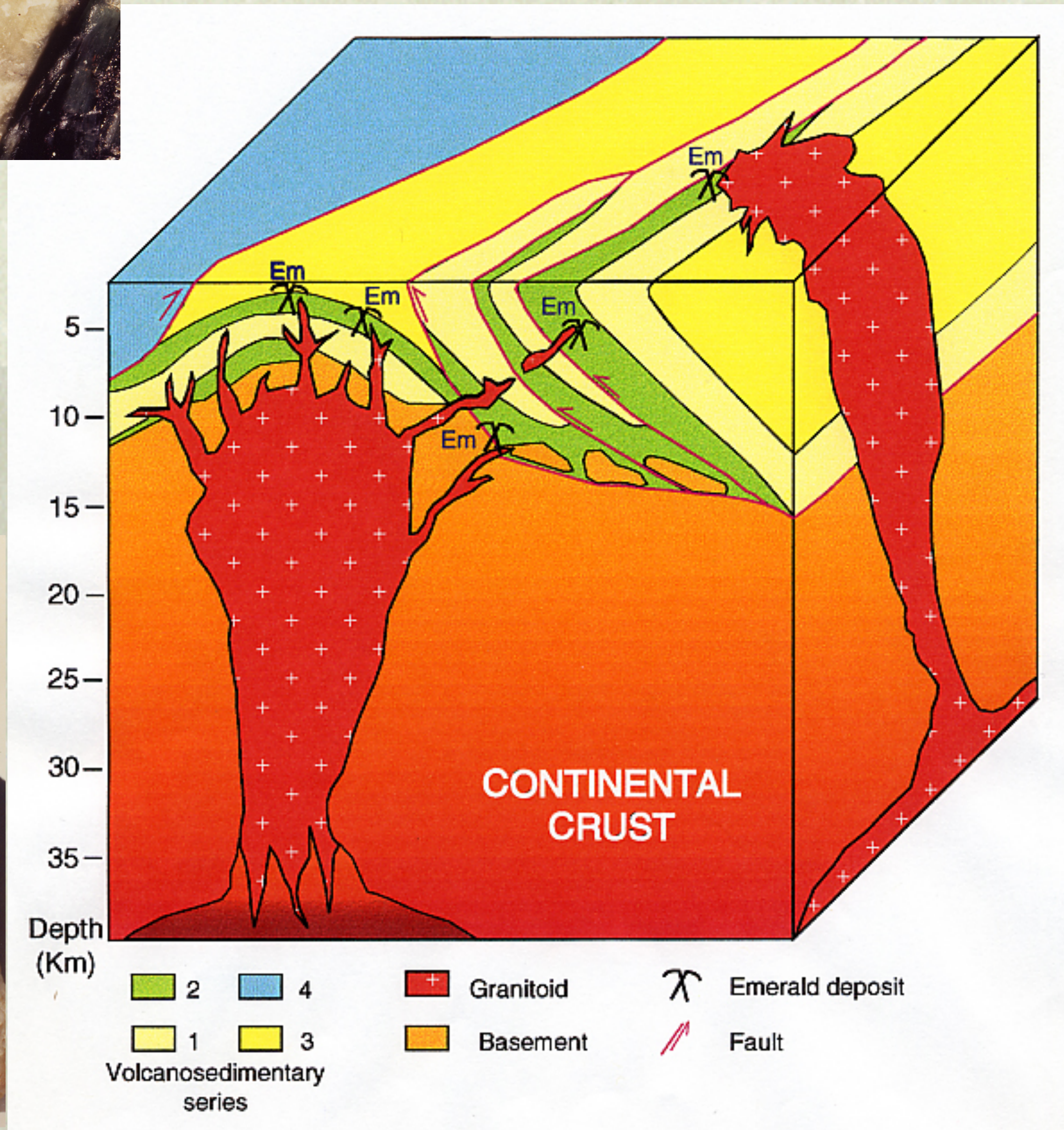
Emerald-bearing biotite schist (Urals)

3.2

Deposits hosted in mafic-ultramafics and related to granitic intrusions and hydrothermalism

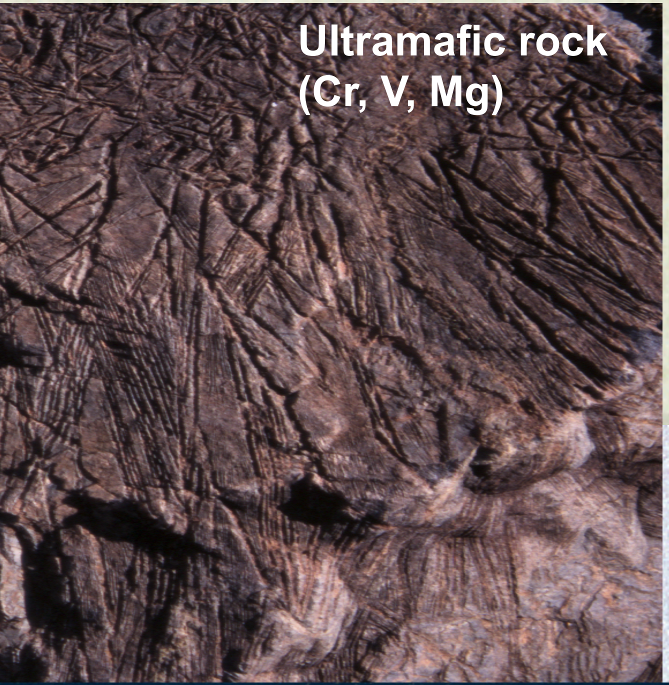
Emerald and granitic intrusions

Desilicated pegmatite

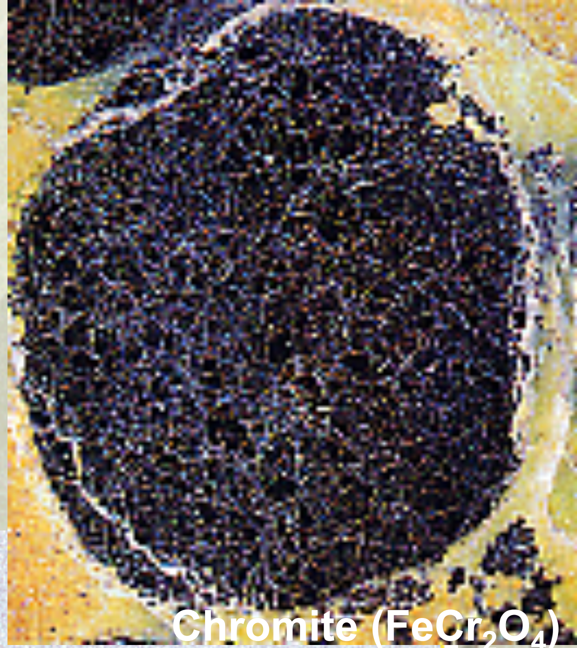


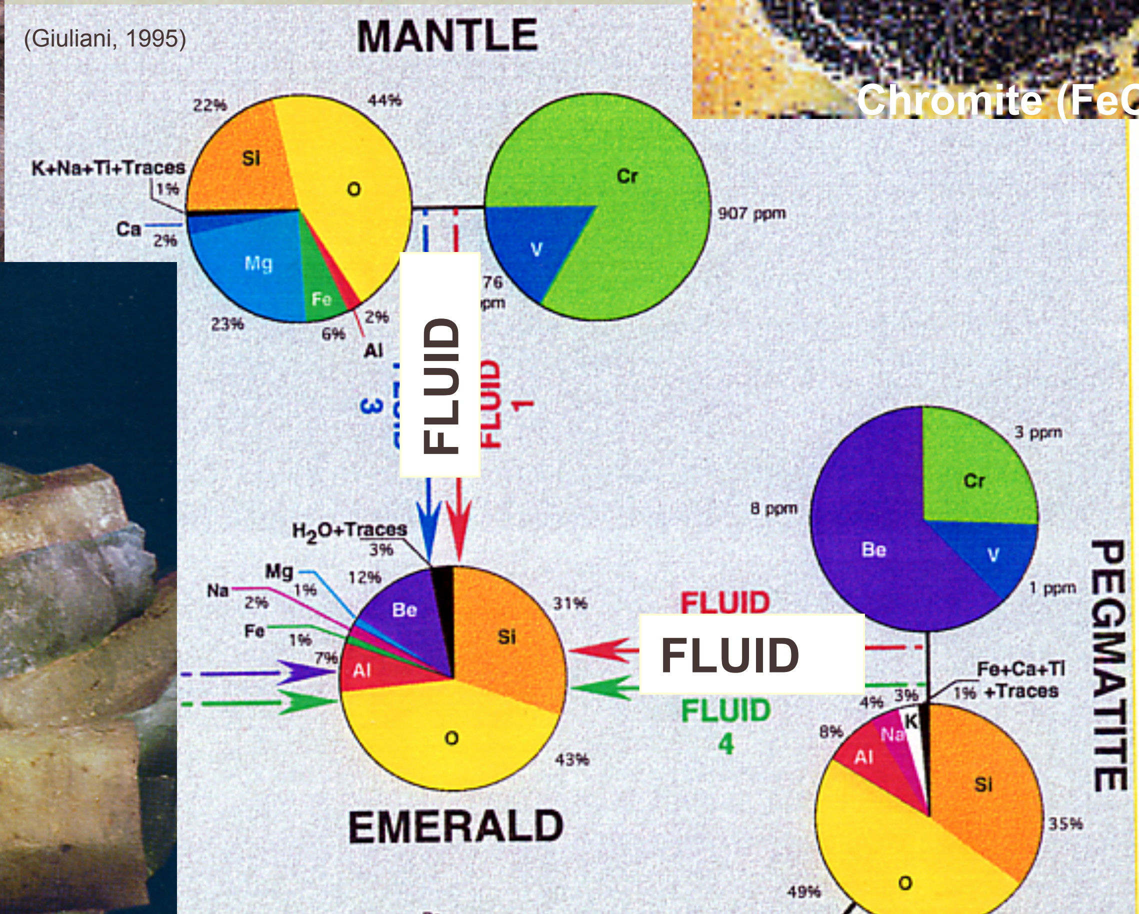
Aplite, pegmatite and quartz veins

3.2.1. Emerald in biotite schist and plagioclasite

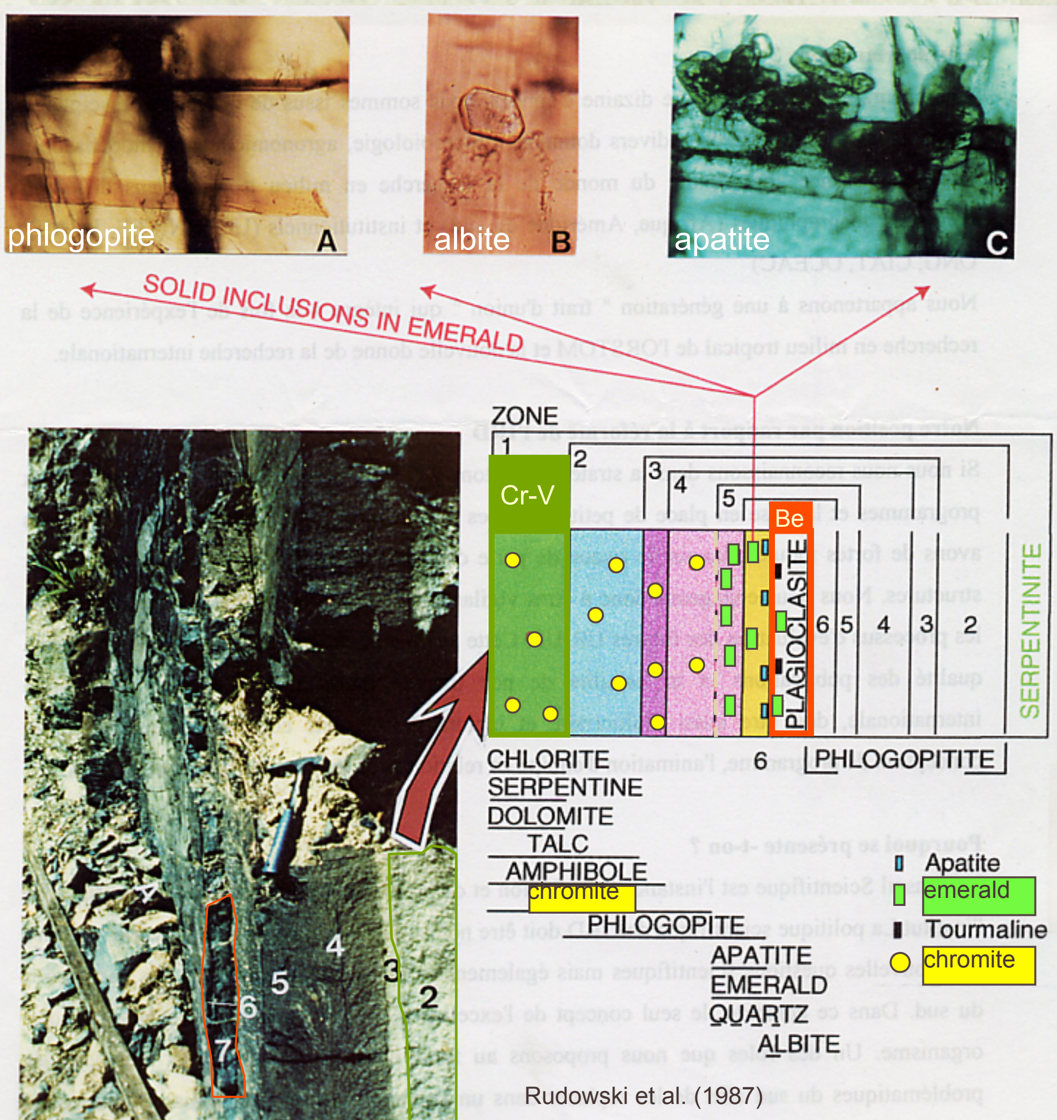


Source of the elements

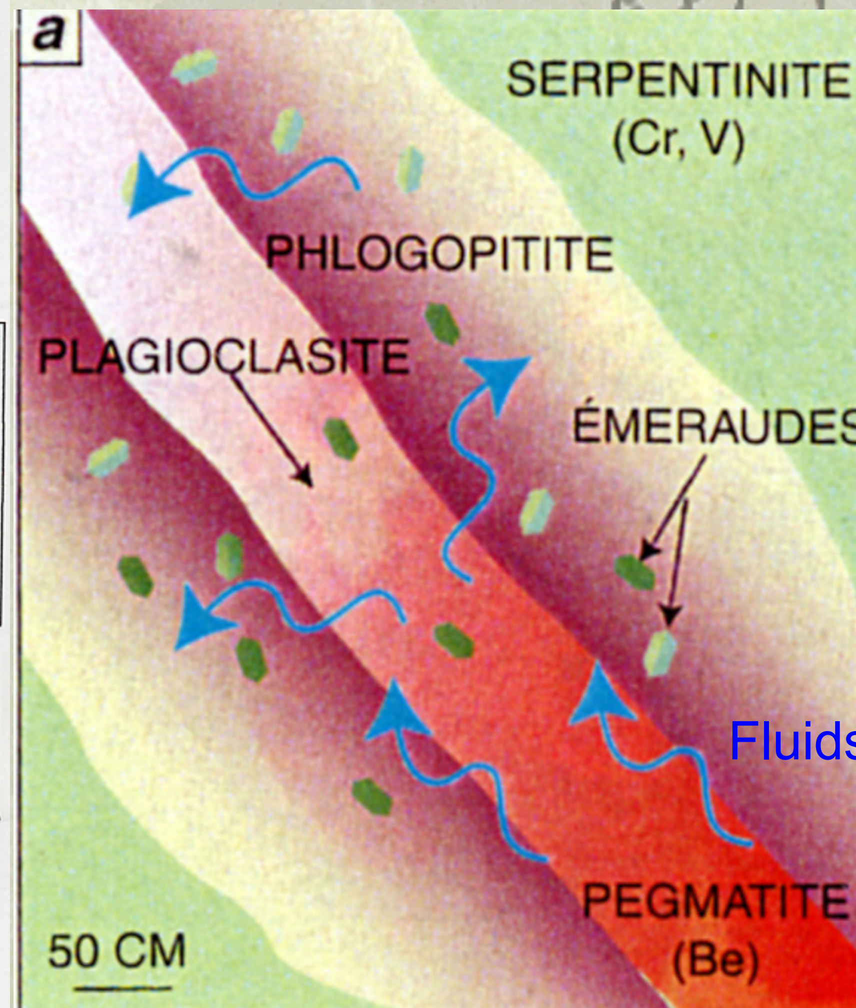




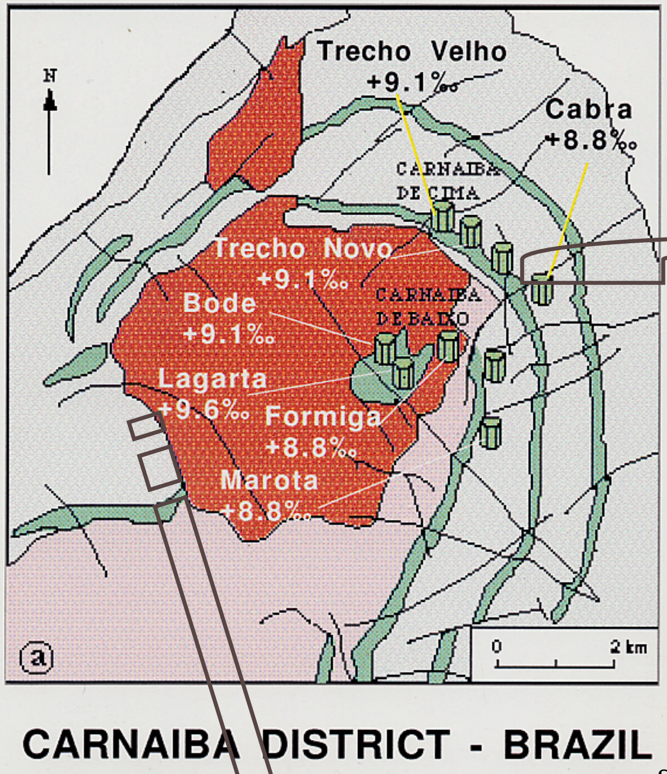
Carnaíba emerald deposit (Brazil):
A metasomatic zoning
due to percolation and fluid-rock interaction



Rudowski et al. (1987)



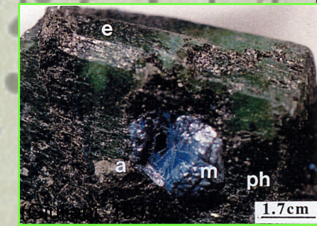
Carnaíba emerald deposit (Brazil)



Pegmatite in UMR

$\delta^{18}O_{emerald}$ = 9.1 ± 0.3 ‰ (n=10)

$\delta D_{emerald}$ = -54 ± 5 ‰ (n= 10)



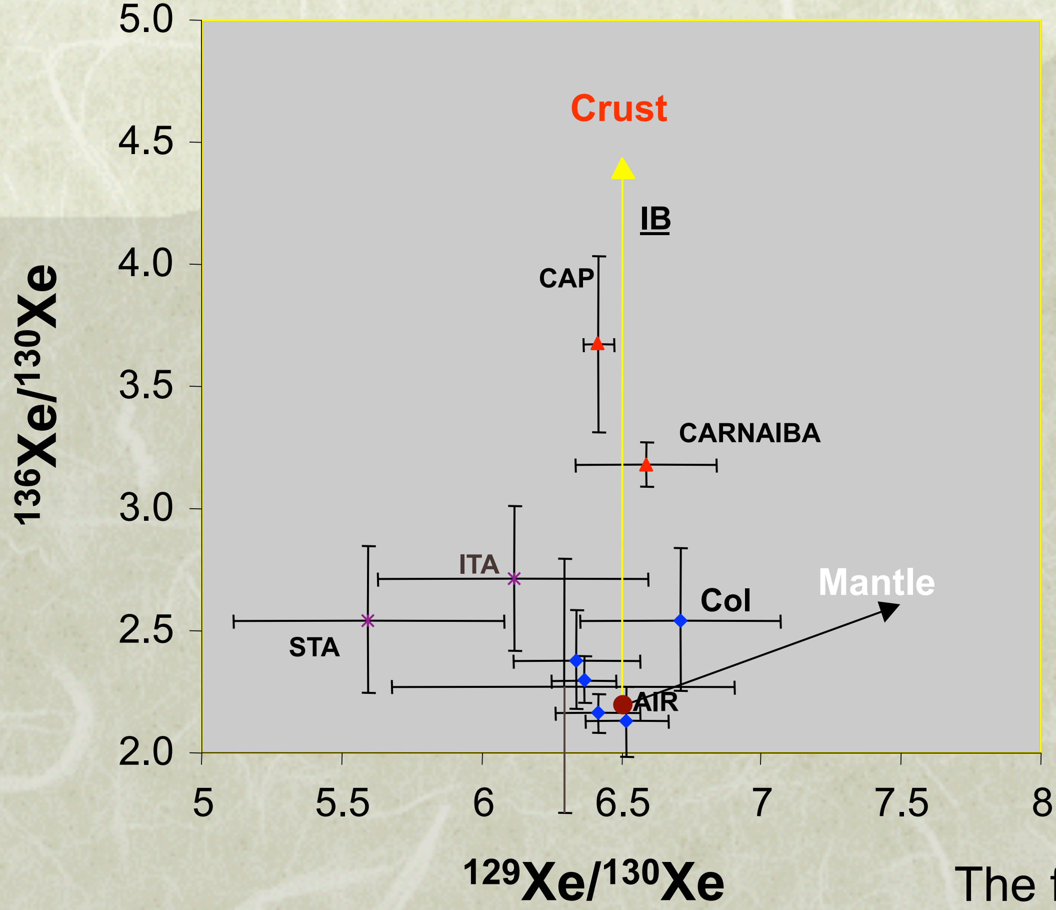
Emerald in plagioclasite and biotite schist

Beryl-bearing pegmatite

Carnaíba emerald deposit (Brazil)

Noble gases: Xenon

^{238}U (Fission) → ^{136}Xe
^{232}Th (Fission) → ^{136}Xe

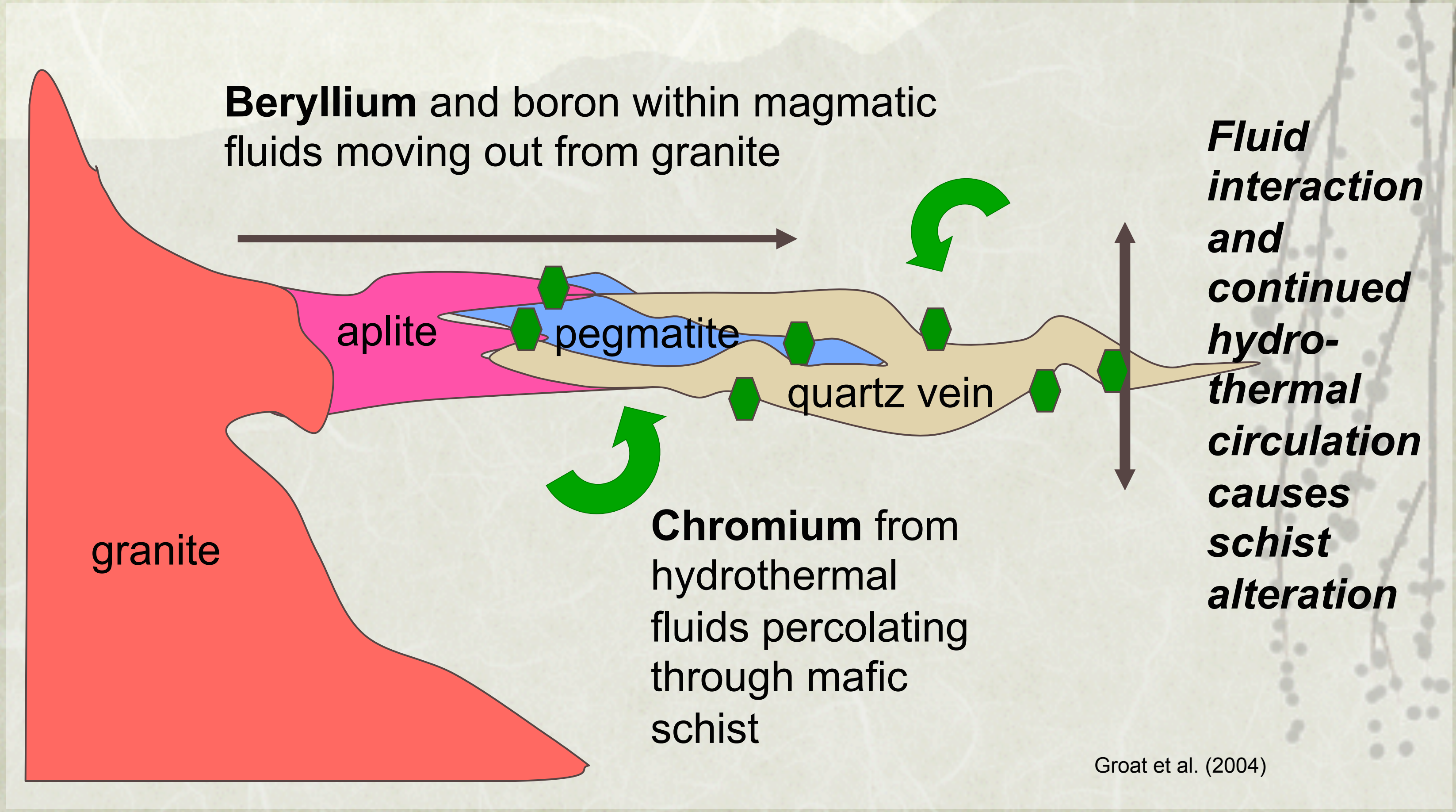


The fluids in emeralds from Carnaiba and Capoierana are ^{136}Xe-rich

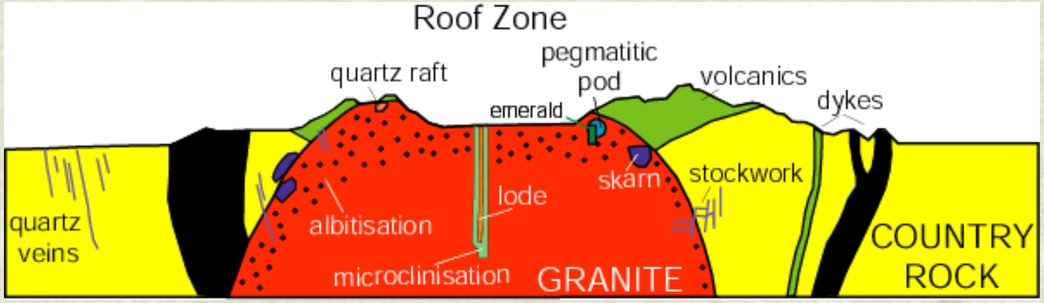
3.2.2 Emerald in quartz, greisen-like veins pegmatite, aplite veins

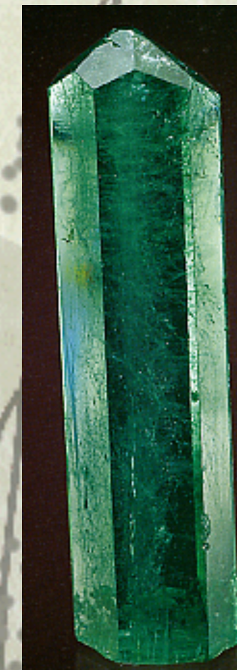
Continued hydrothermal circulation from the granite to the quartz vein

TSA DA GLISZA (Canada)

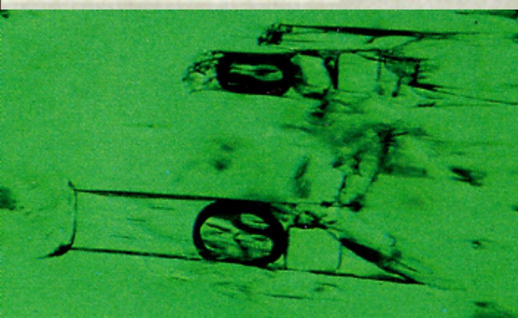


Magmatic brines and gemstones: Nigerian emeralds

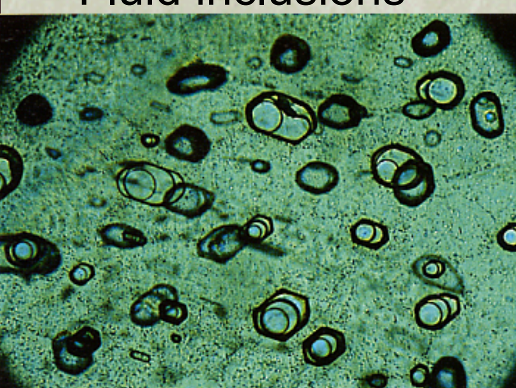


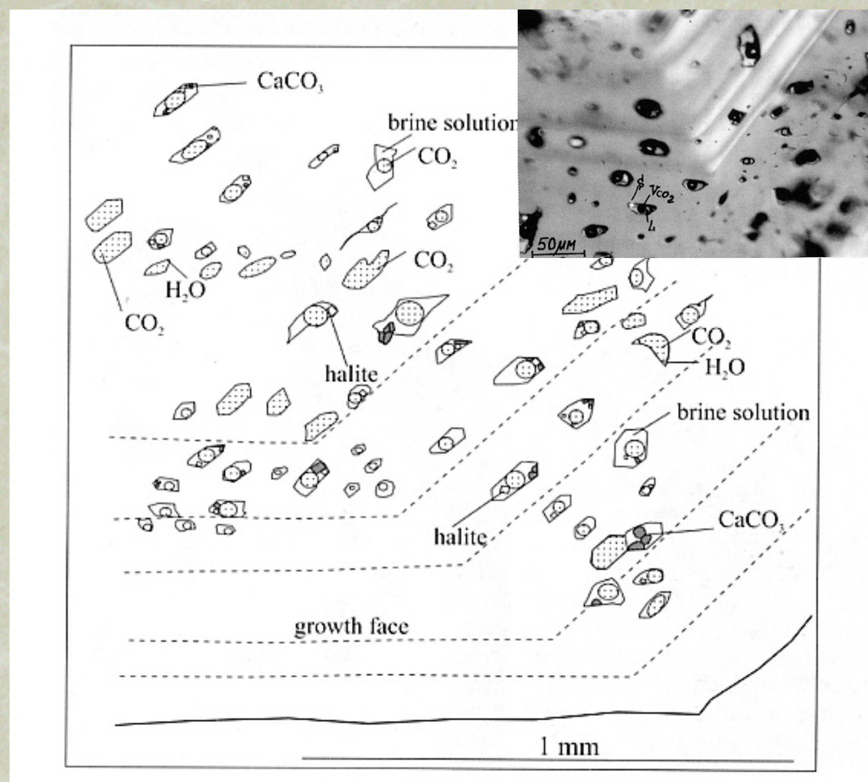


Intragranitic emerald-bearing pegmatite pods: Source of chromium ?



Fluid inclusions





Vapnik & Moroz (2000)

T ~ 400-450°C P ~ 0.2-0.3 kb

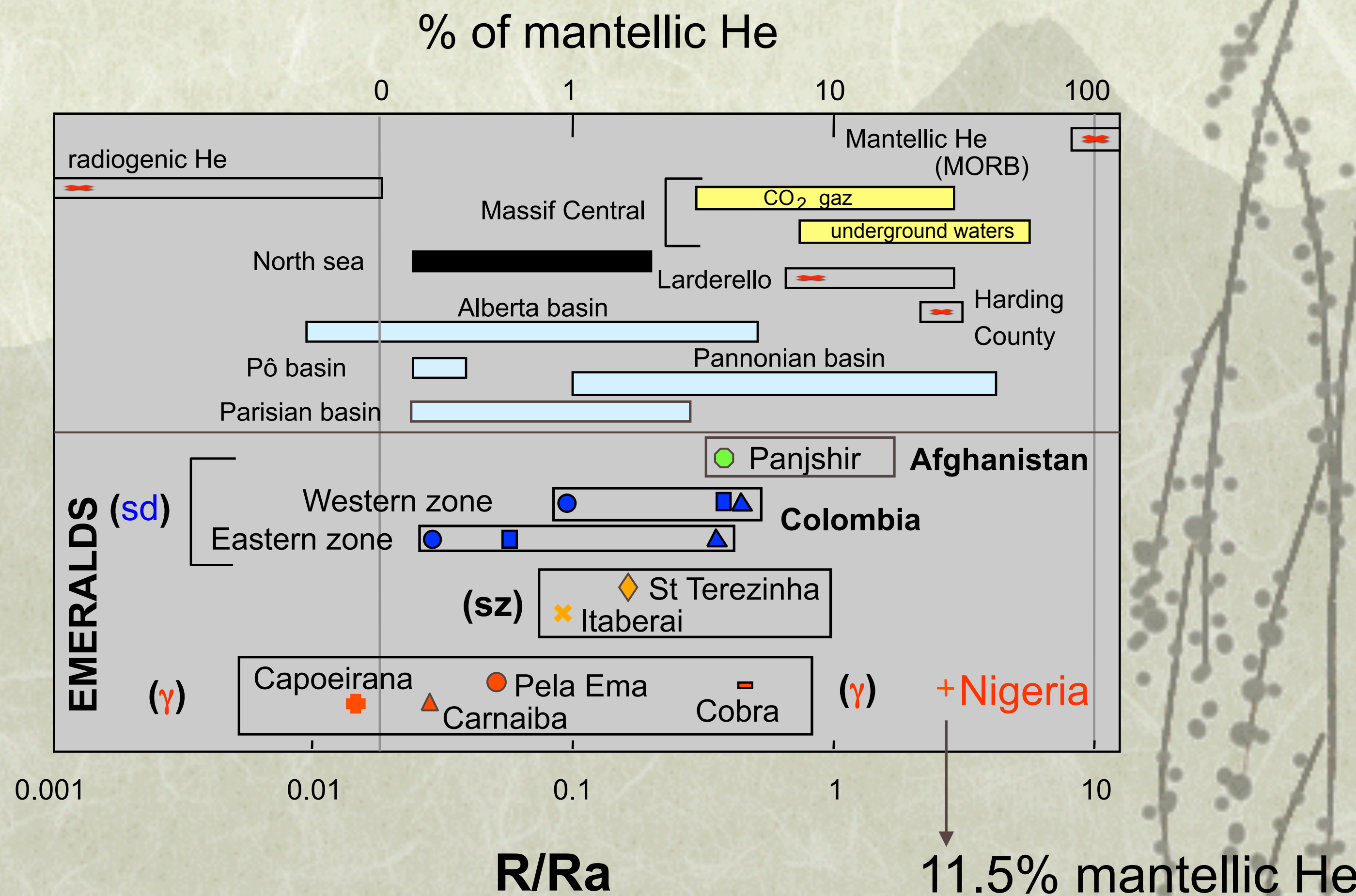
$\delta^{18}O$ = 9.5‰ (n= 2)
δD ~ -49‰

Oxygen
and hydrogen isotopes

Giuliani et al. (1998)

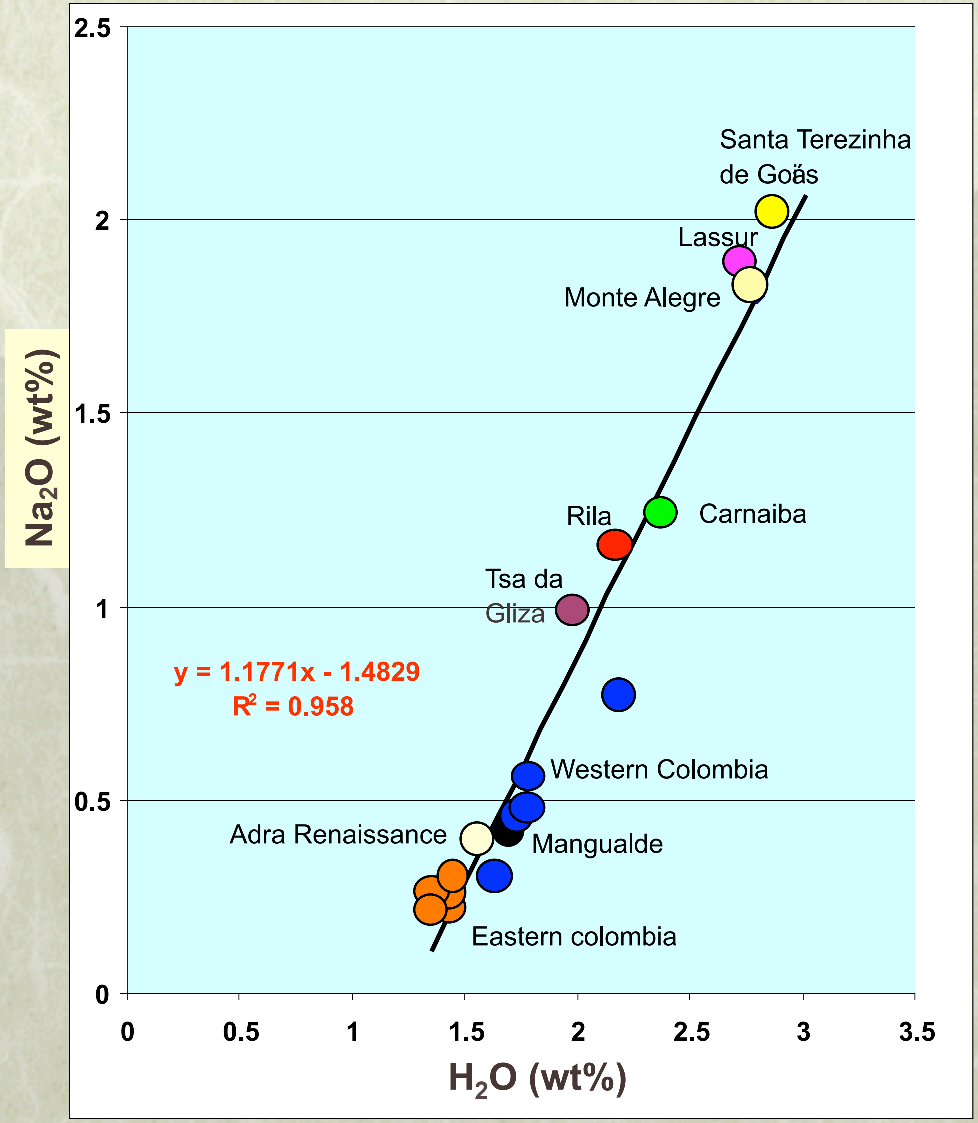
Origin of brines ?

$^3He/^4He$ in emerald from Nigeria



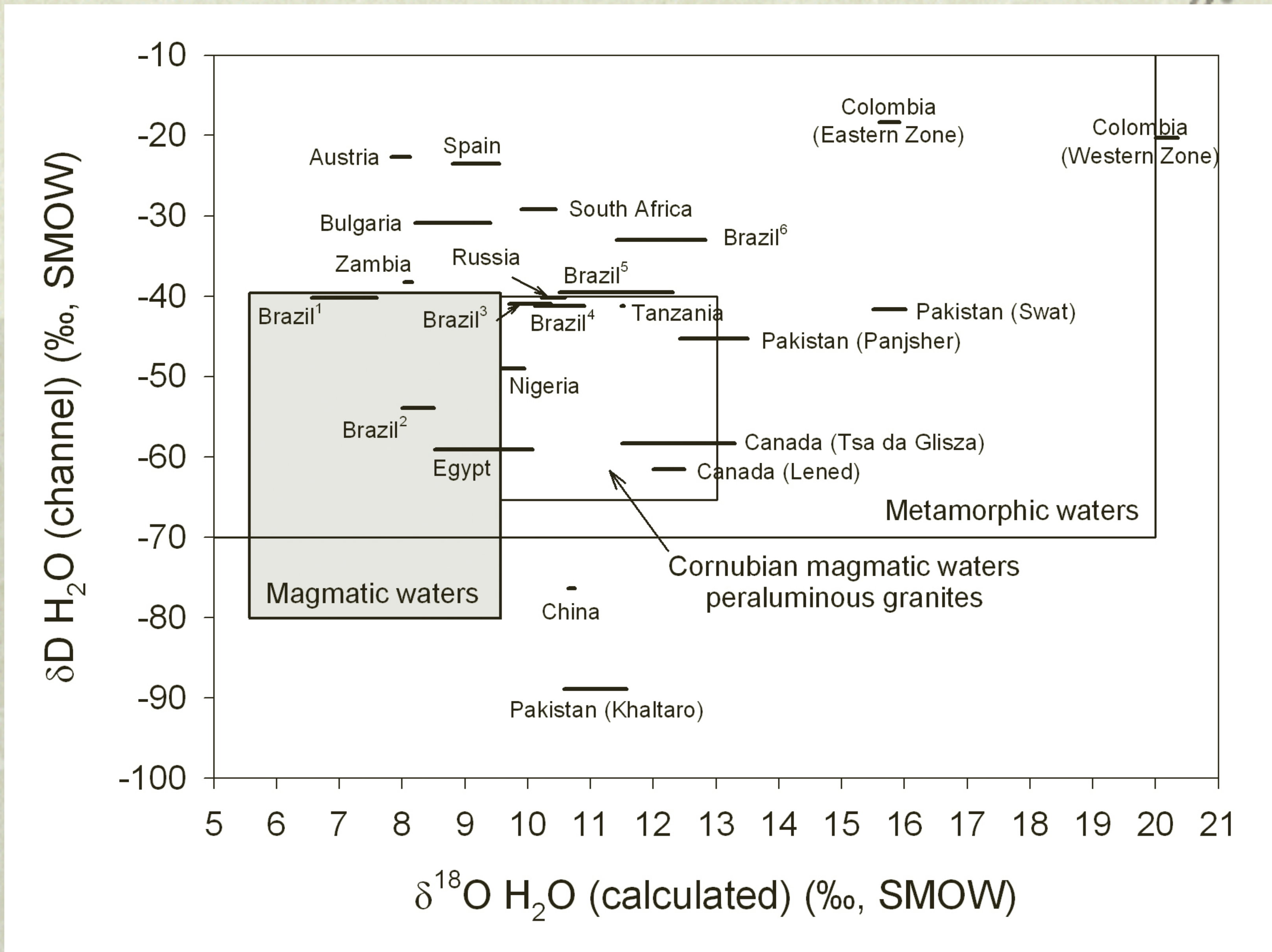
$R/Ra = {}^3He/^4He$ of emerald / $^3He/^4He$ of the air ($Ra = 1.386 \times 10^{-6}$)

H_2O content (wt%) in the channels of emerald



Giuliani, 2006)

Origin of the mineralizing fluids



3.2.3 Corundum in plagioclasite vein

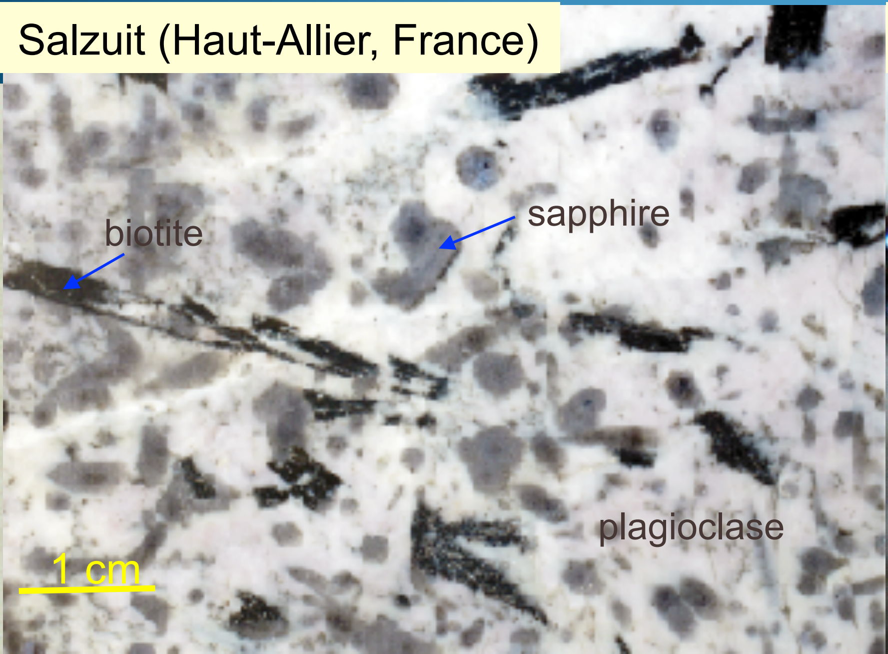
Dequartzification and feldspathisation of the pegmatites: the “plumasites”

$$KAlSi_3O_8 + \underline{Na}^{+}_{aq} = NaAlSi_3O_8 + \underline{K}^{+}_{aq}$$

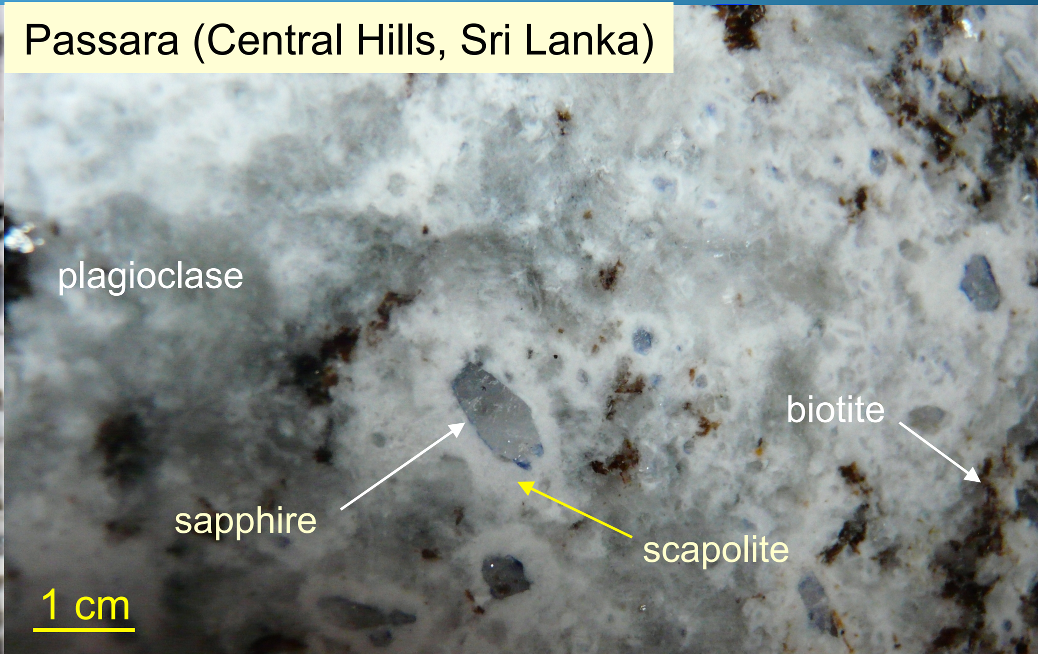
$$CaAl_2Si_2O_8 + 4SiO_2 + 2\underline{Na}^{+}_{aq} = 2NaAlSi_3O_8 + \underline{Ca}^{2+}_{aq}$$

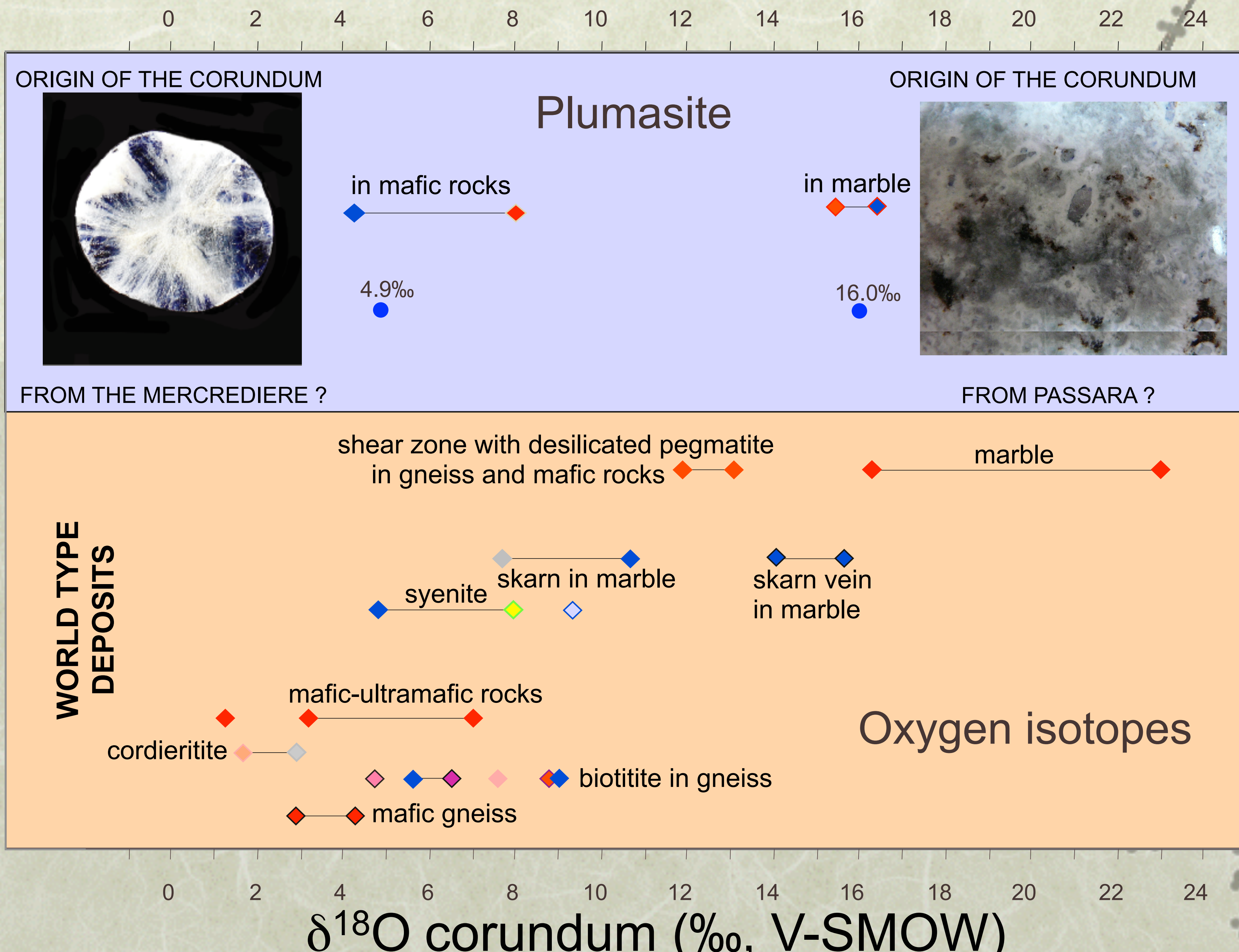
$$CaAl_2Si_2O_8 + SiO_2 + \underline{Na}^{+}_{aq} + 4H^{+} = NaAlSi_3O_8 + \underline{Ca}^{2+}_{aq} + Al^{3+} + 2H_2O$$

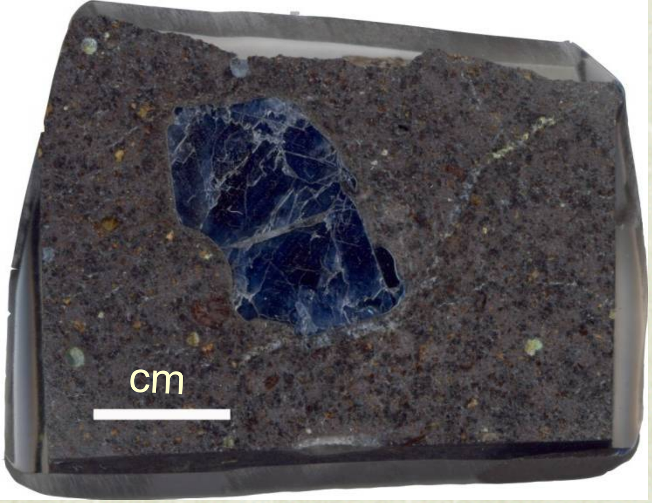
Salzuit (Haut-Allier, France)



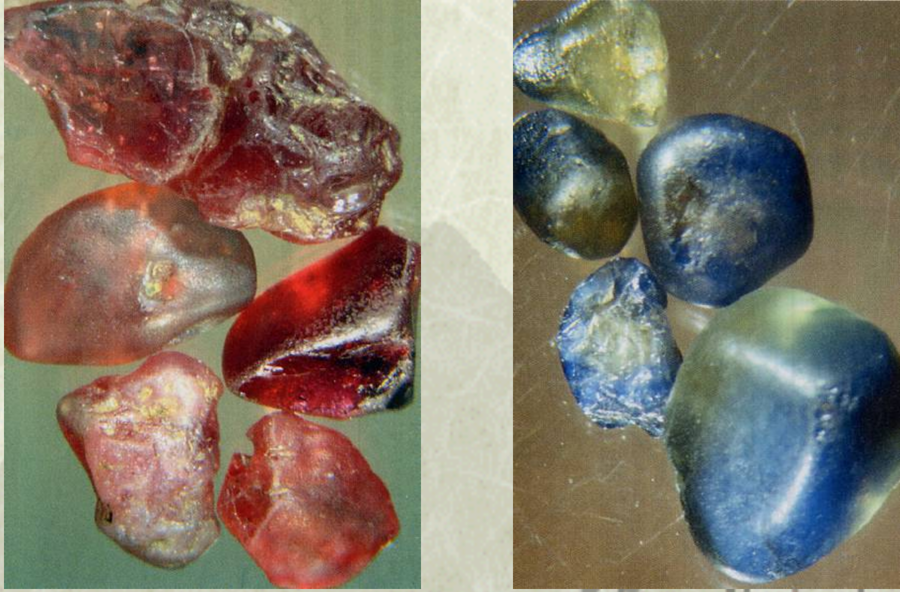
Passara (Central Hills, Sri Lanka)




0 2 4 6 8 10 12 14 16 18 20 22 24
ORIGIN OF THE CORUNDUM
Plumasite
ORIGIN OF THE CORUNDUM
in mafic rocks
in marble
4.9‰
16.0‰
FROM THE MERCREDIERE ?
FROM PASSARA ?
shear zone with desilicated pegmatite
in gneiss and mafic rocks
marble
WORLD TYPE
DEPOSITS
skarn in marble
syenite
skarn vein
in marble
mafic-ultramafic rocks
cordieritite
Oxygen isotopes
biotitite in gneiss
mafic gneiss
0 2 4 6 8 10 12 14 16 18 20 22 24
δ18O corundum (‰, V-SMOW)



Xenocryst of sapphire in basalt (China)

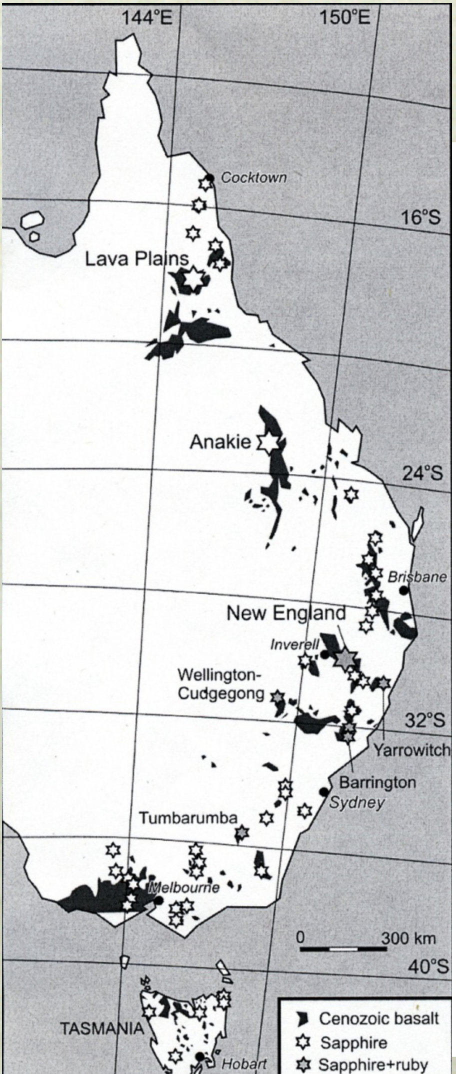


Rubies and BGY-sapphires from Australian placers

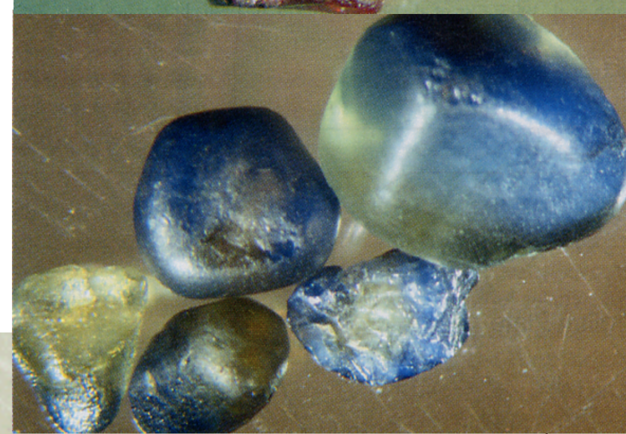
3.3

Deposits hosted in alkali basalts and mafic dykes

AUSTRALIA: an example of corundum deposits related to alkali basalts

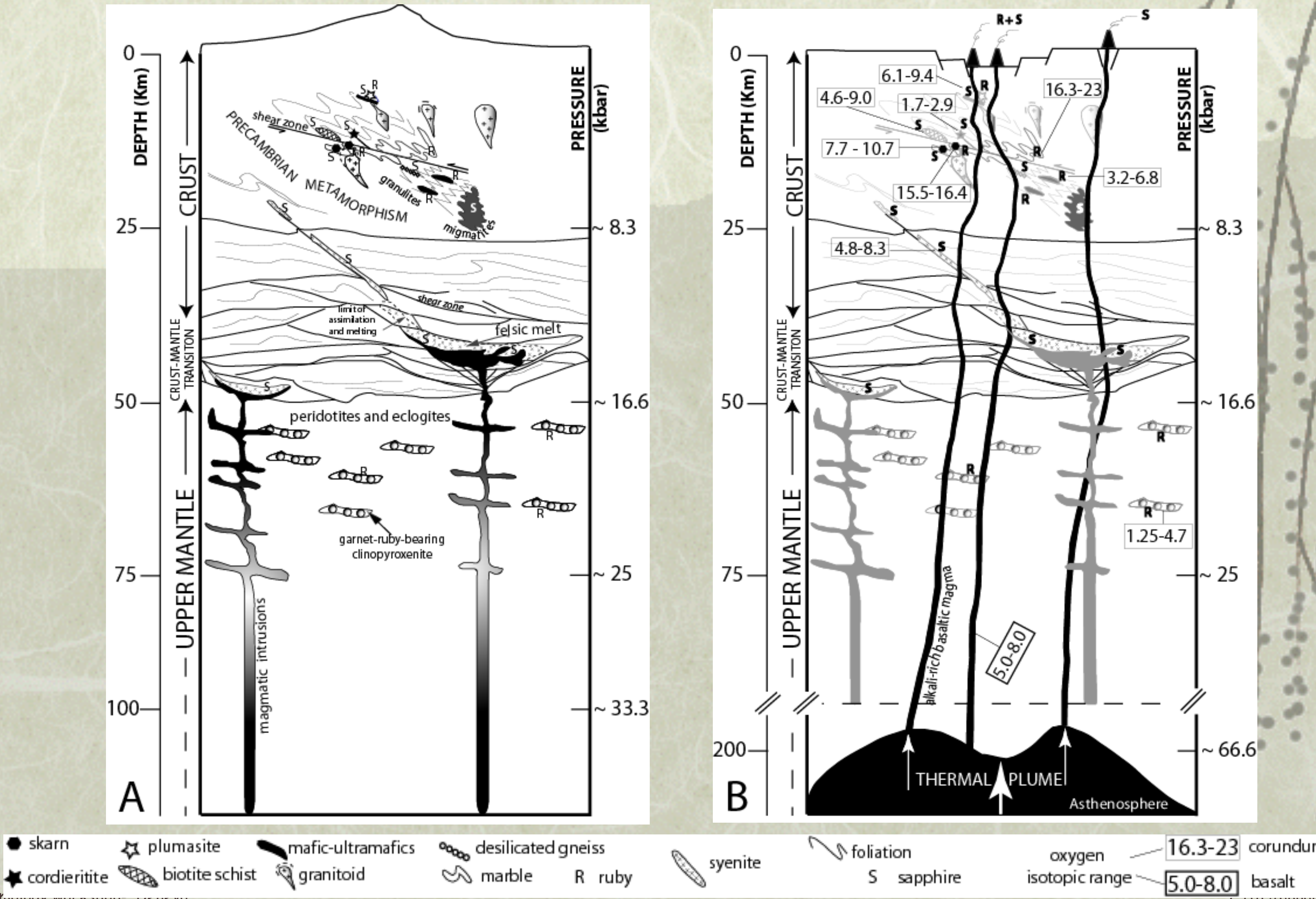


Sutherland et al. (1998, 2003, 2008)
Graham et al. (2008)



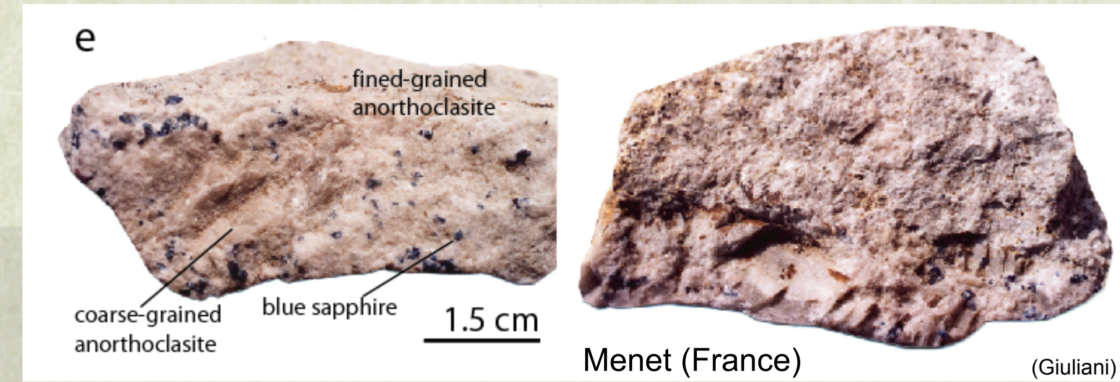
Sapphire and ruby- related basalt (Worldwide)
Genetic Model

Giuliani et al. (2009)

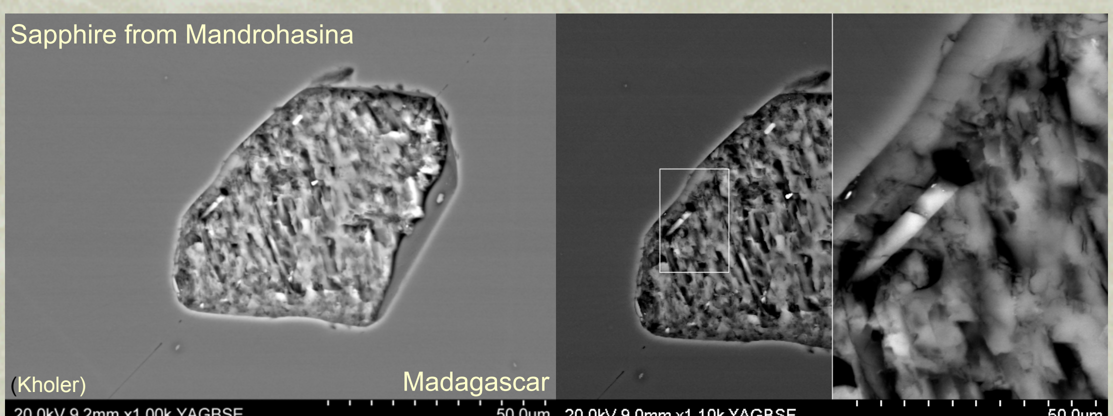


Sapphire-related basalt (Worldwide)
Genetic Model

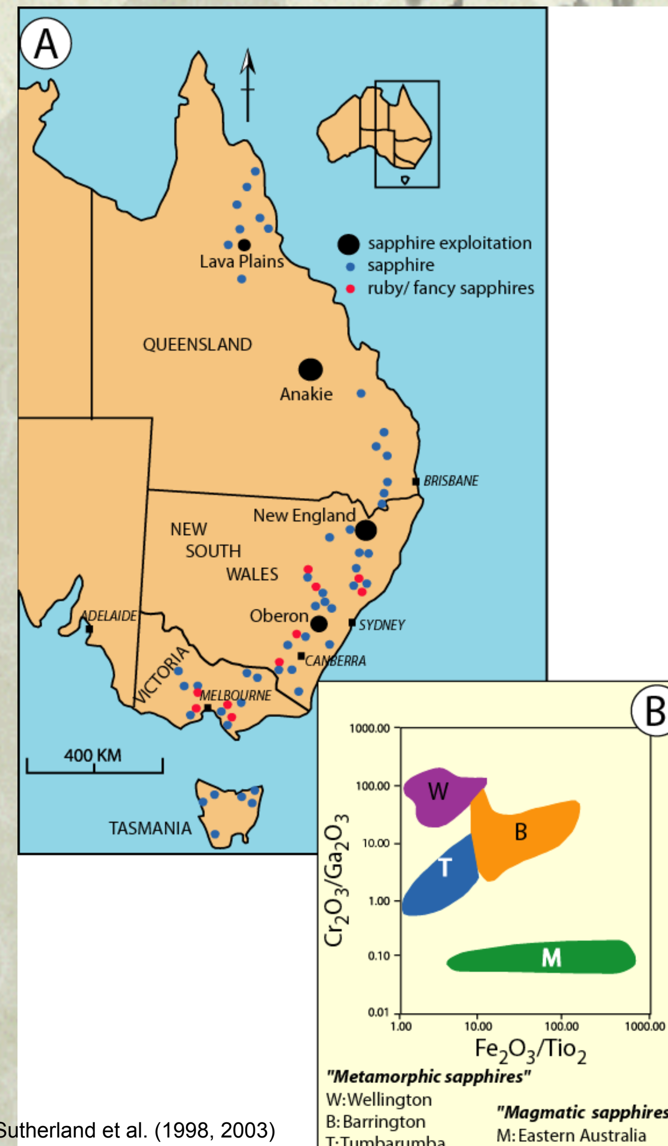
Magmatic



Sapphire-bearing syenite (anorthoclasite)



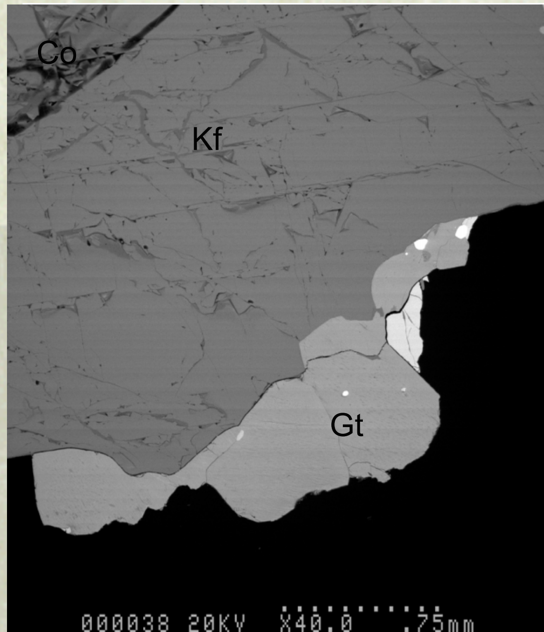
Nb-Ti-Ta-U, Y+REE solid inclusions

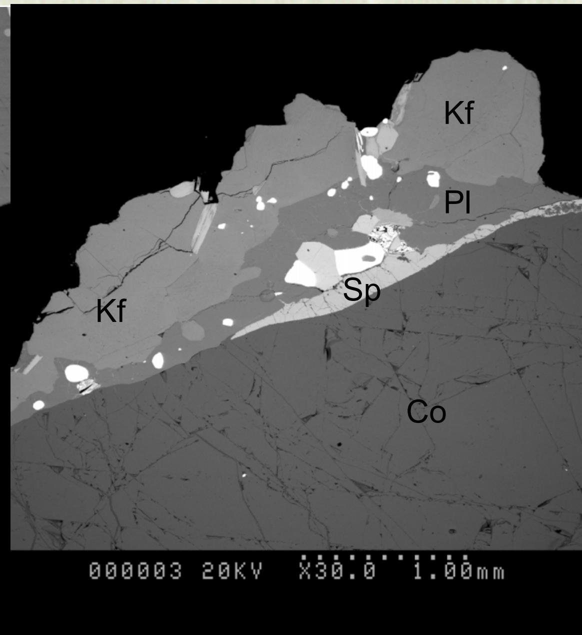


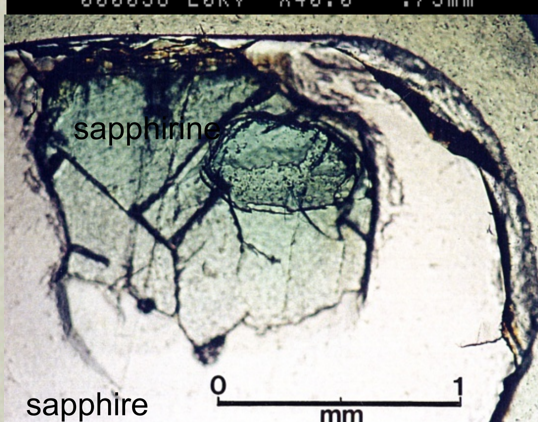
Sutherland et al. (1998, 2003)

Sapphire-related basalt (Worldwide) Genetic Model

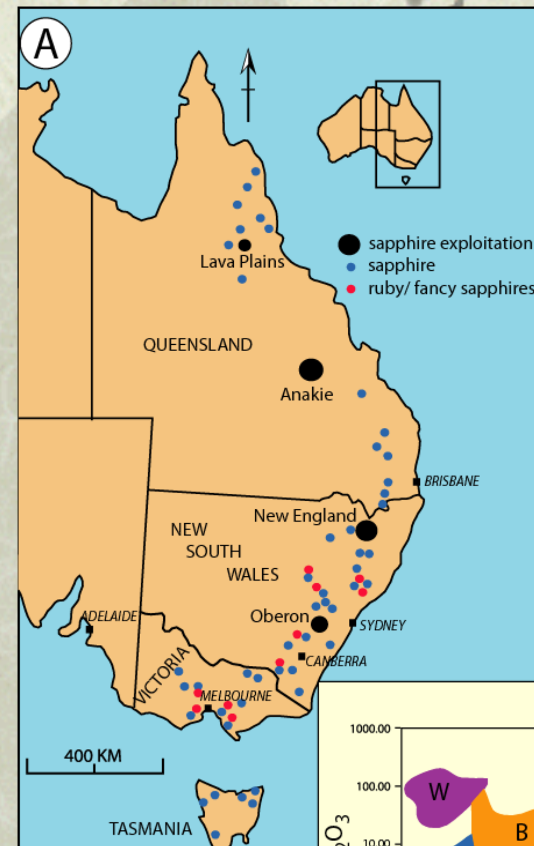
Magmatic versus metamorphic

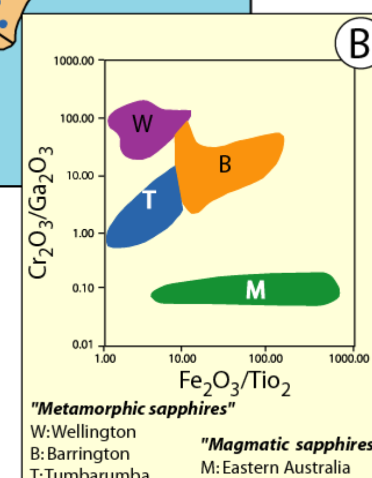






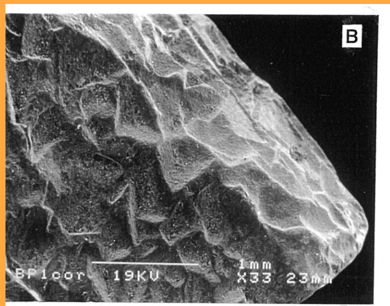
Metamorphic sapphires
(Rakotosamizanany et al., 2009)



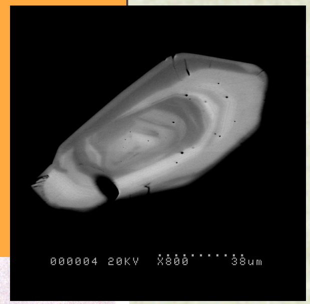


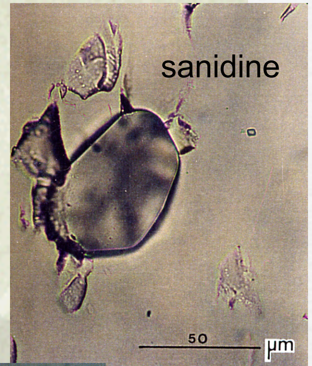
Sutherland et al. (1998, 2003)

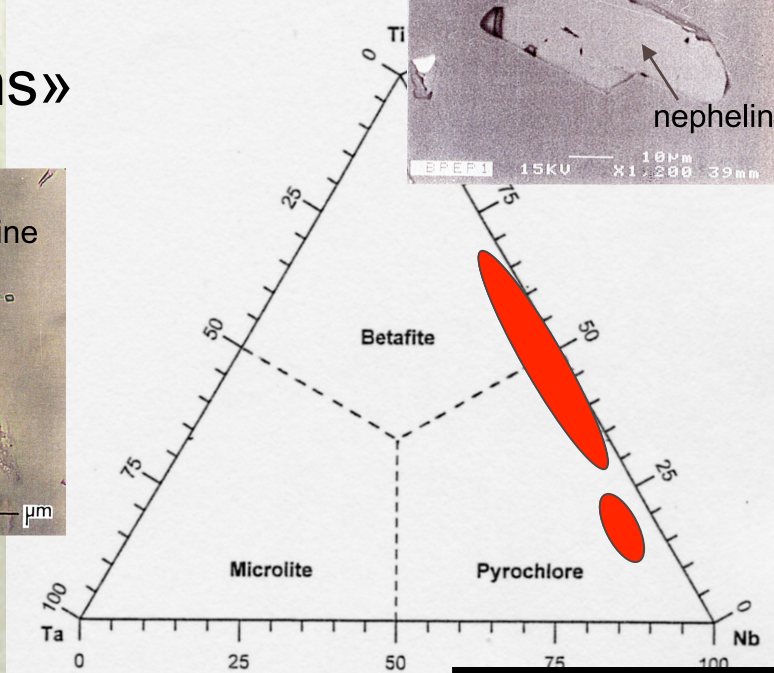
The «basaltic corundums»

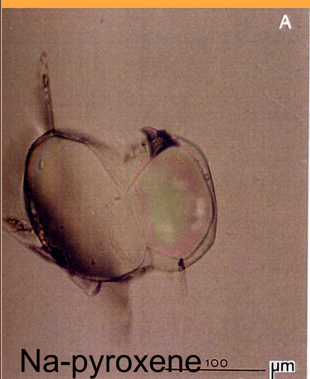


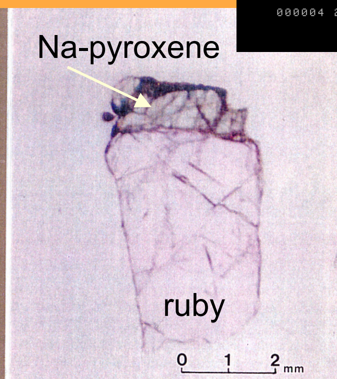
Xenocrysts: corrosion effect

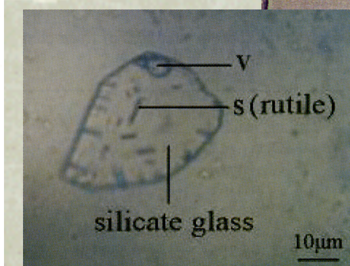


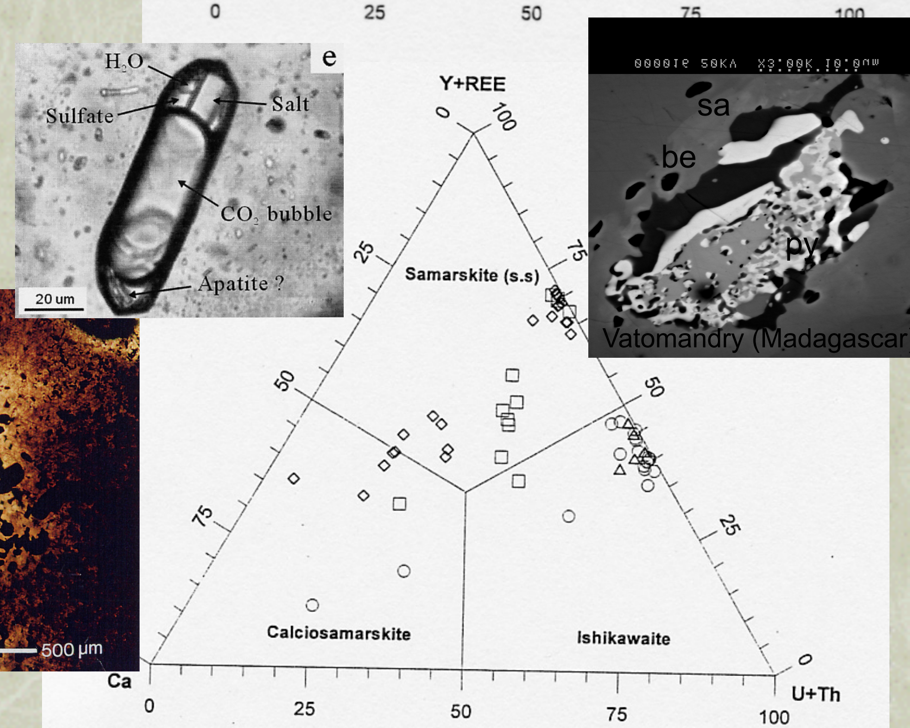


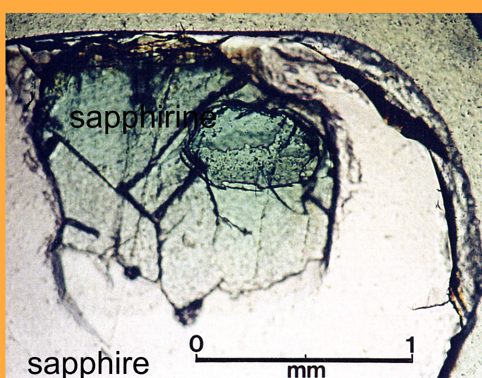


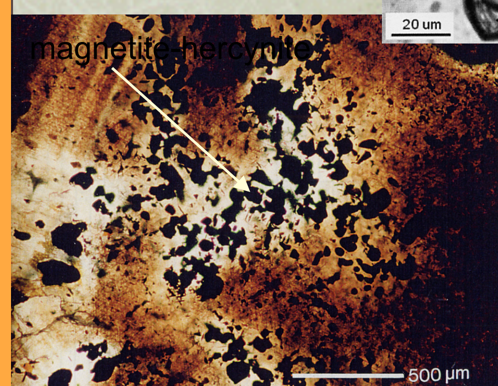












Metamorphic paragenesis

Magmatic paragenesis

Ruby-related basalt (Worldwide)
Genetic Model

The Soamiakatra deposit
(Madagascar)

(Rakotosamizanany, 2009)

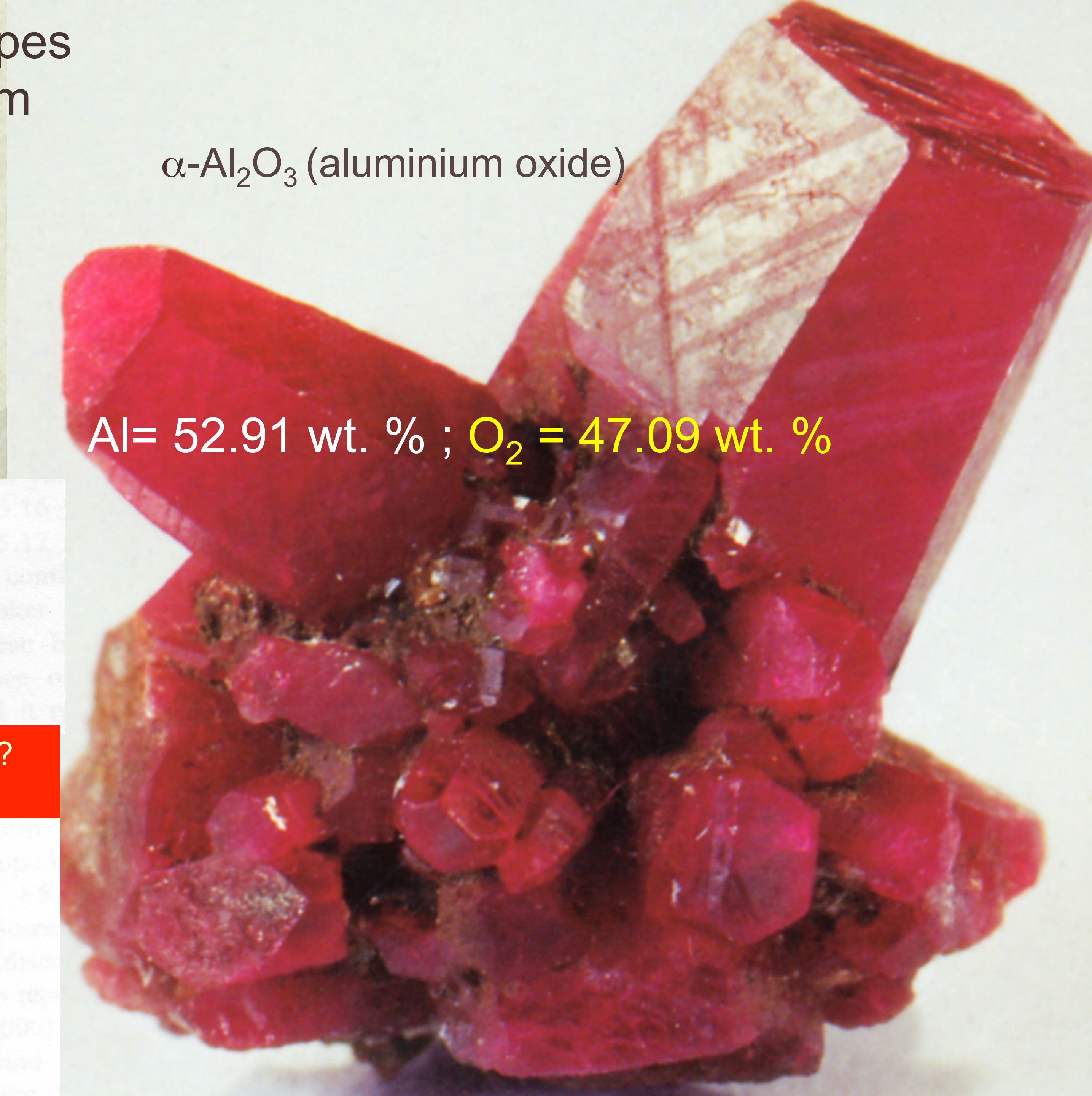
Enclaves of metagabbros
and pyroxenites

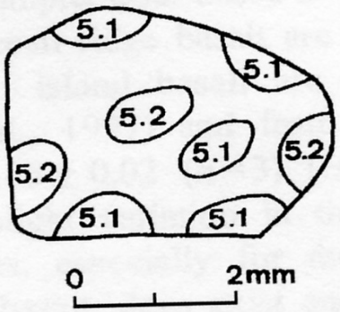
P ~ 20 kb and T ~ 1100°C

Oxygen isotopes in corundum

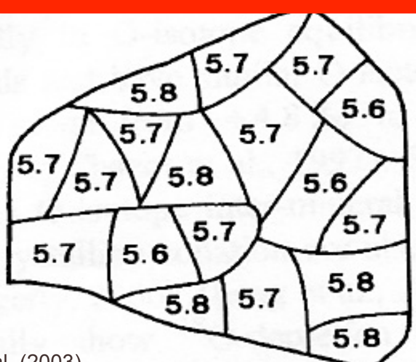
α-Al_2O_3 (aluminium oxide)

Al= 52.91 wt. % ; O_2 = 47.09 wt. %

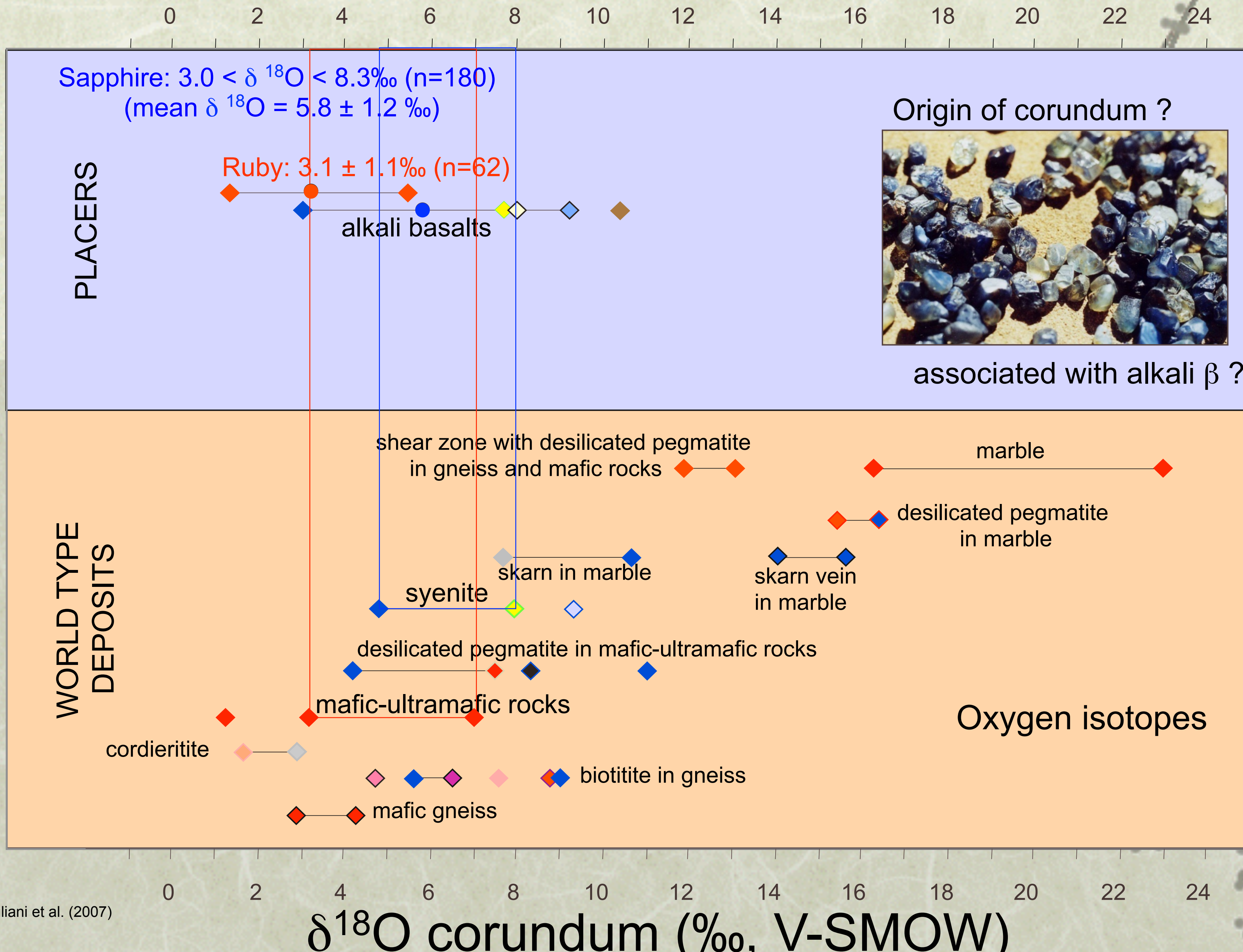




Isotopic homogeneity ?
Yes

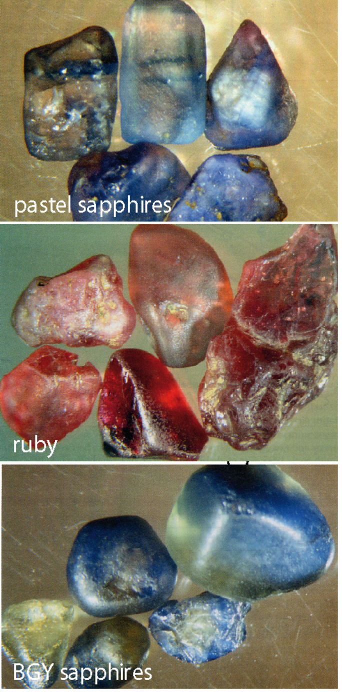


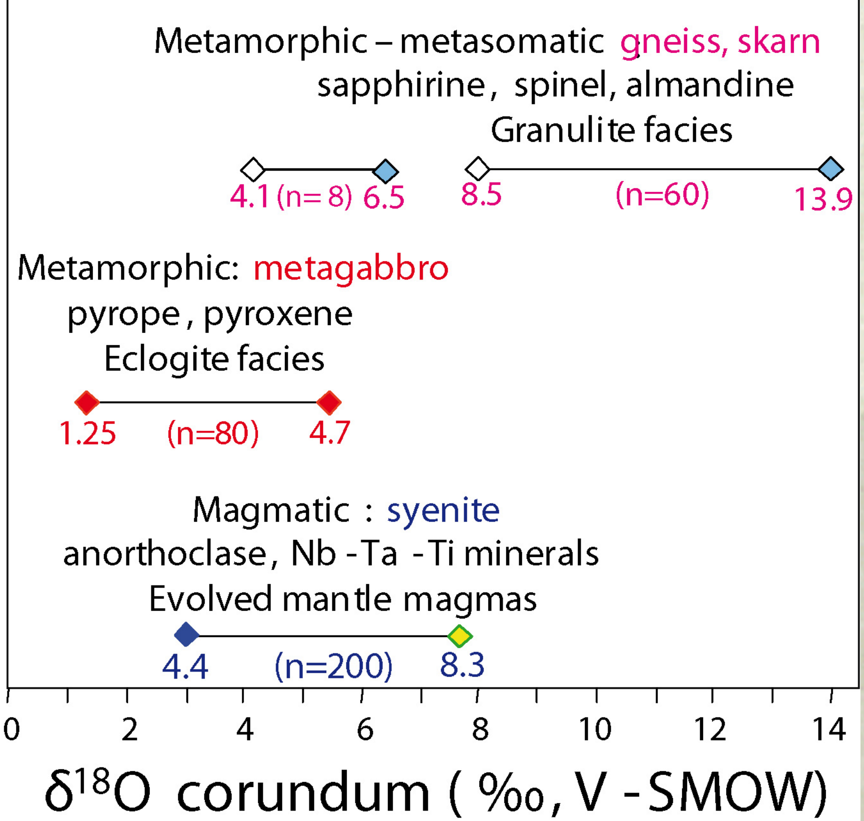
Yui et al. (2003)



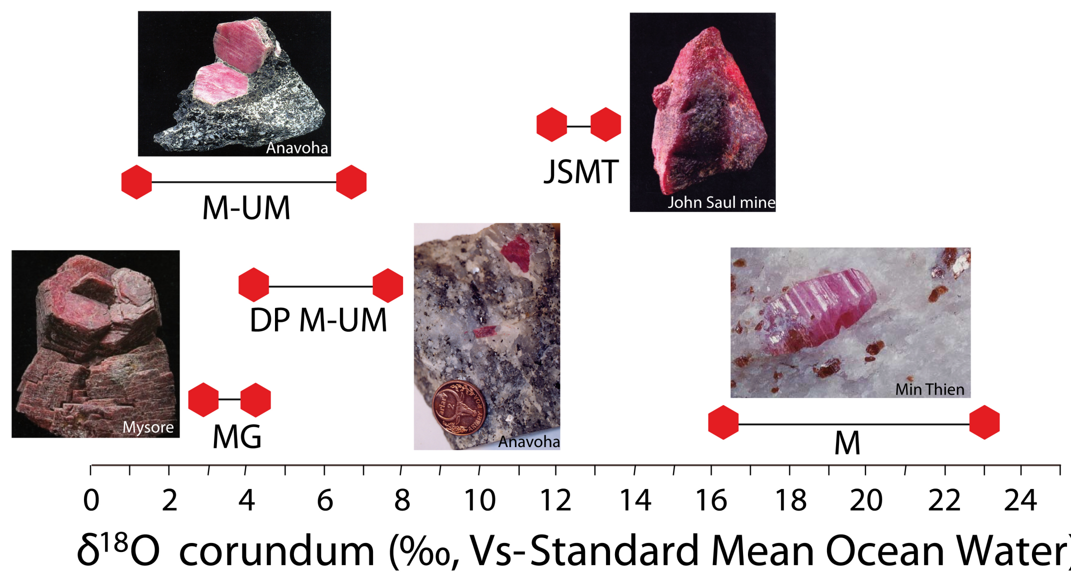
Giuliani et al. (2007)

The origin of corundum in alakali basalt





The geologic origin of ruby worldwide



4

Conclusions

Emerald is rare but corundum is frequent due to its setting and hardness (placers). Geologically, two types of contrasted minerals: silica-rich environment and silica-poor environment.

Two types of contrasted genesis excepted for some important types:

Emerald and ruby related to metamorphosed platformal sediments have a common history regarding their chromophorous elements (Cr and V), but also their mother fluid originating from the dissolution or fusion of evaporites. Importance of stable isotopes regarding their geological formation and origin.

Metasomatism and fluid/rock interacation is the main processus for the formation of emerald deposits in mafic-rocks and the corundum-pegmatite type related deposit.

Magmatic corundum related to alkali basalts are the most important in term of production. But rubies and sapphires are xenocrysts of magmatic and metamorphic origin carried up by the magma.