UNIVERSIDADE DE SÃO PAULO

GEOCIÊNCIAS USP

PETROGRAFIA DE MINÉRIOS (GSA 0501)

ÓXIDOS DE Cr e de Sn-W

DEPARTAMENTO DE GEOLOGIA SEDIMENTAR E AMBIENTAL

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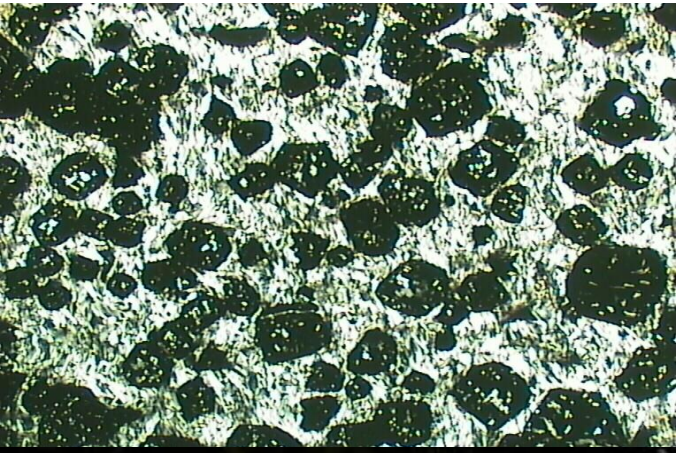
CONTEXTO GEOLÓGICO DOS ÓXIDOS DISCUTIDOS...

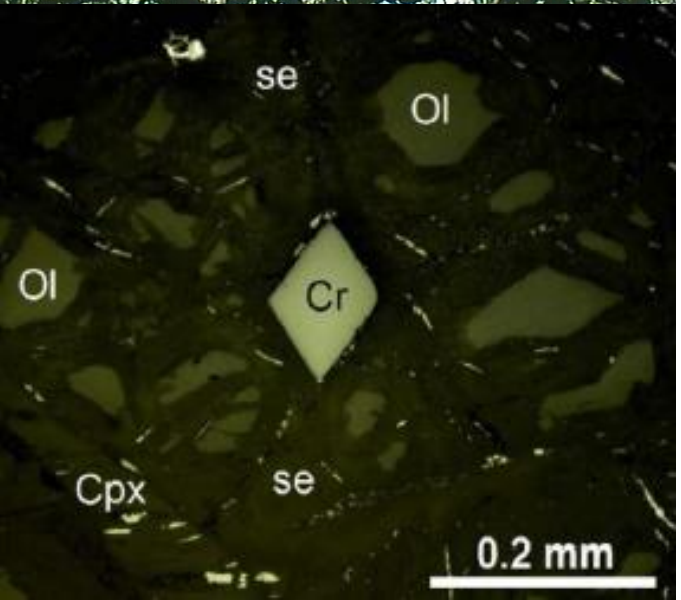
CROMITA

- Vinculada a depósitos magmáticos (filiação magmática), derivados da cristalização de magmas máficos e ultramáficos.
- Depóstios de cromita estratiforme e de cromita podiforme. Também pode ocorrer como material detrítico em aluviões e pláceres, embora não perfasa zonas mineralizadas.

ÓXIDOS DE Sn-W

- Relacionados a sistemas magmático-hidrotermais do tipo greisens e, portanto, derivados da cristalização de magmas graníticos alcalinos (granitos tipo S e/ou tipo A).
- A cassiterita também pode ocorrer em sistemas minerais sedimentares do tipo placer (placers estaníferos).





SISTEMA Cr-Fe-O

ESPINÉLIOS

Fórmula Geral → $M^{2+}O.(M^{3+})_2O_3$ → Me_3O_4

M^{2+} = Mg, Fe, Mn, Zn

M^{3+} = Al, Cr, Fe, Ti, Mn

Fe^{2+} Cr_2 O_4

$(Fe,Mg)(Cr,Al)_2O_4$

Ou

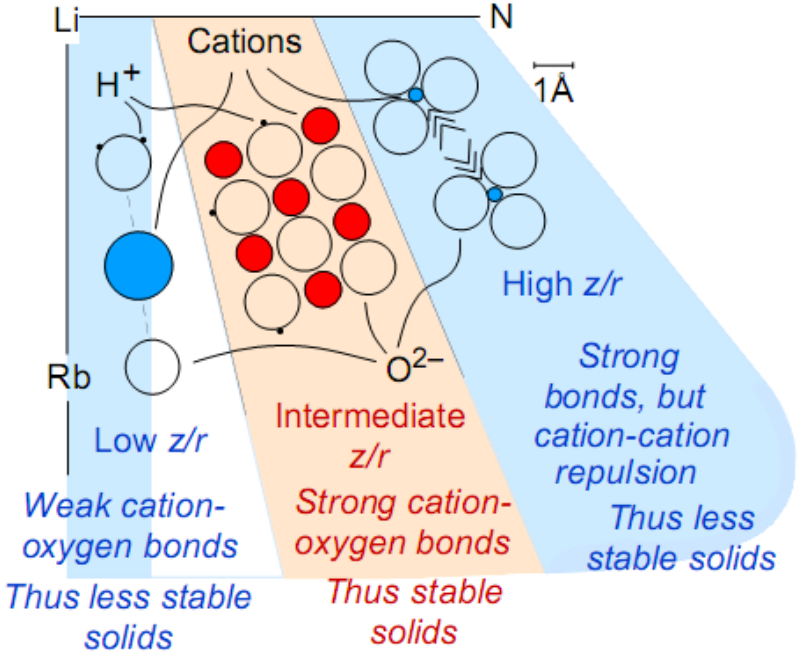
$Fe^{2+}Cr_2O_4$

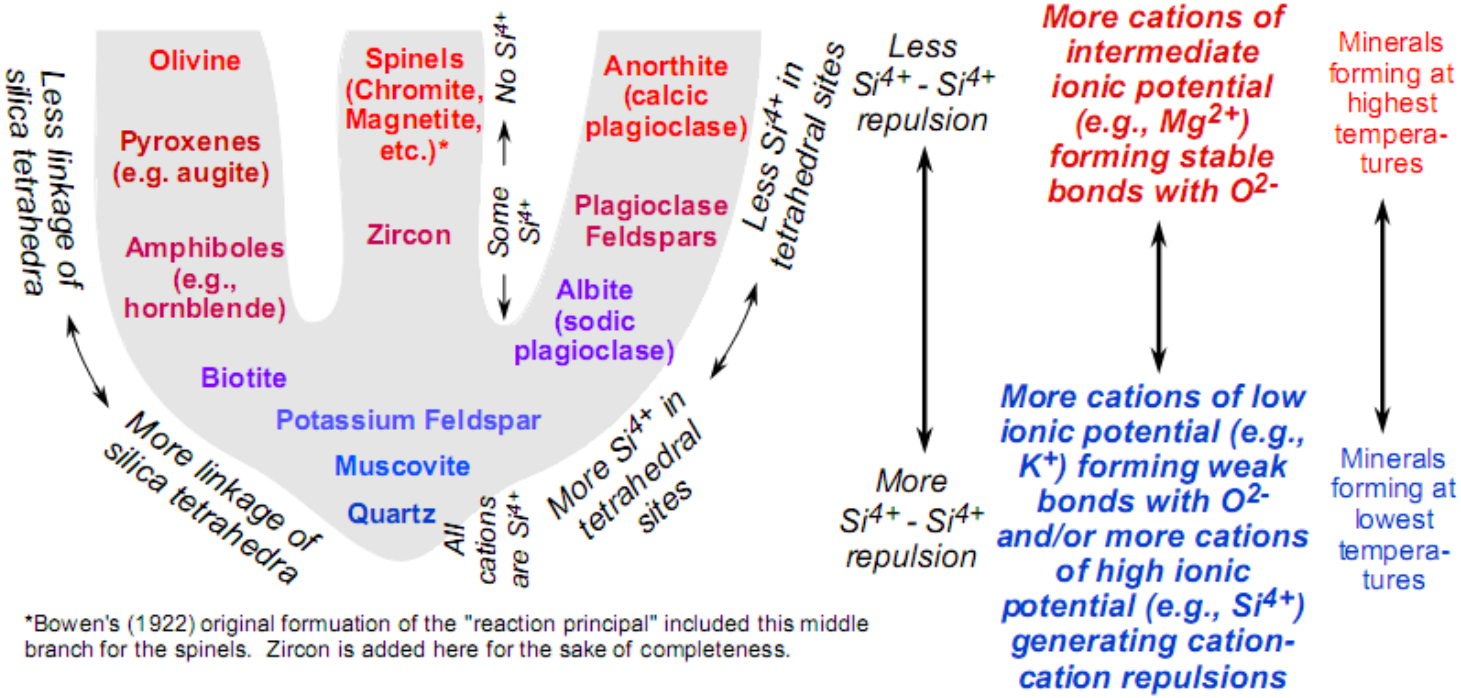
...logo, a cromita é pertencente ao sistema cúbico (isométrico) e, portanto, isotrópica.

Tendência generalizada de cristalização de silicatos em rochas ígneas.

Olivine
Pyroxene
Amphibole
Biotite
K-feldspar
Muscovite
Quartz
Chromite
Magnetite
Albite
Anorthite

Conceptual model of the behavior of oxides of hard (and intermediate) cations

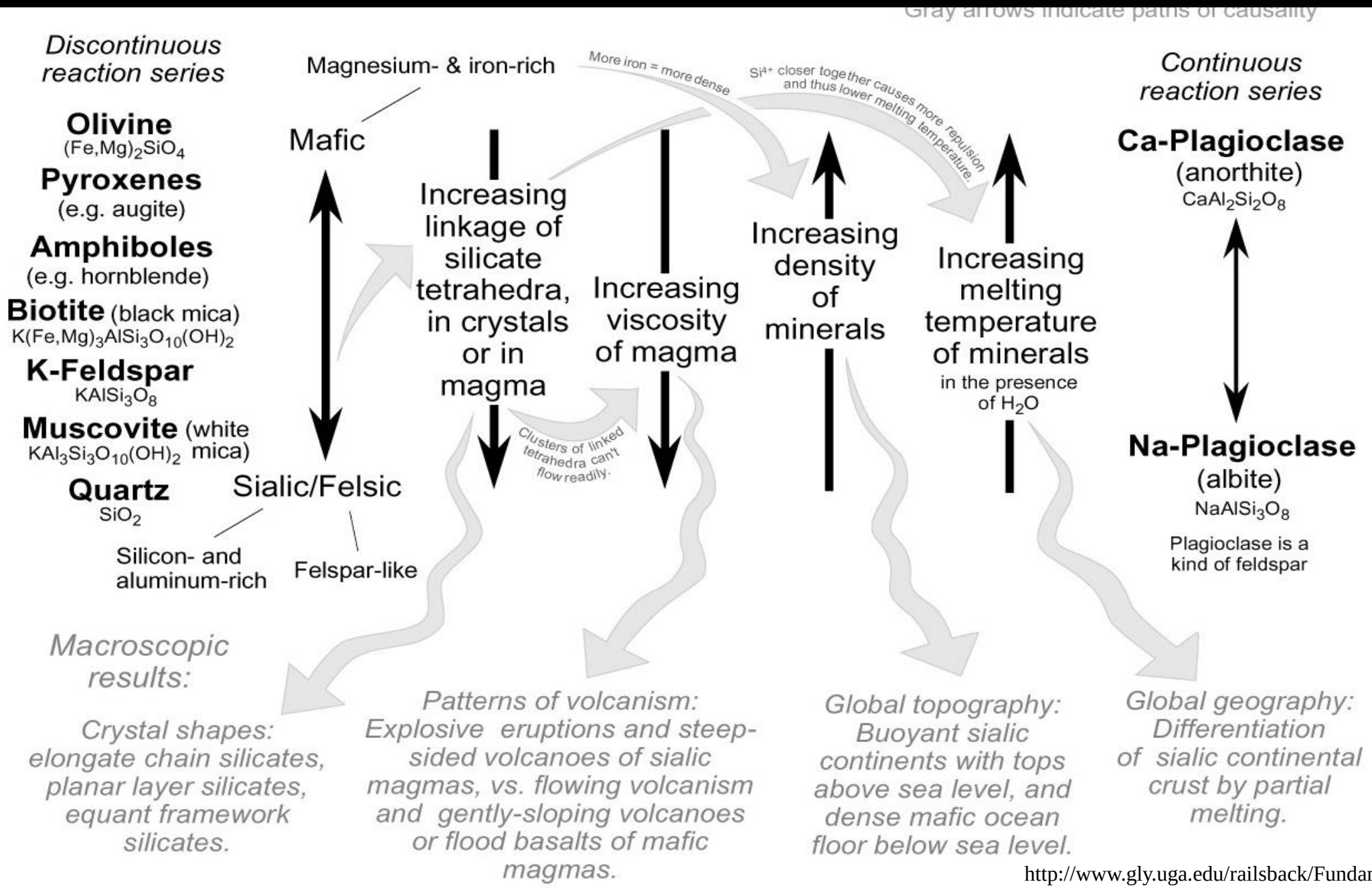




*Bowen's (1922) original formuation of the "reaction principal" included this middle branch for the spinels. Zircon is added here for the sake of completeness.

Fonte:
http://www.gly.uga.edu/rail'sback/FundamentalsIndex.html

Tendência generalizada de cristalização de silicatos em rochas ígneas.



Fonte:
http://www.gly.uga.edu/railsback/FundamentalsIndex.html

SISTEMA Cr-Fe-O

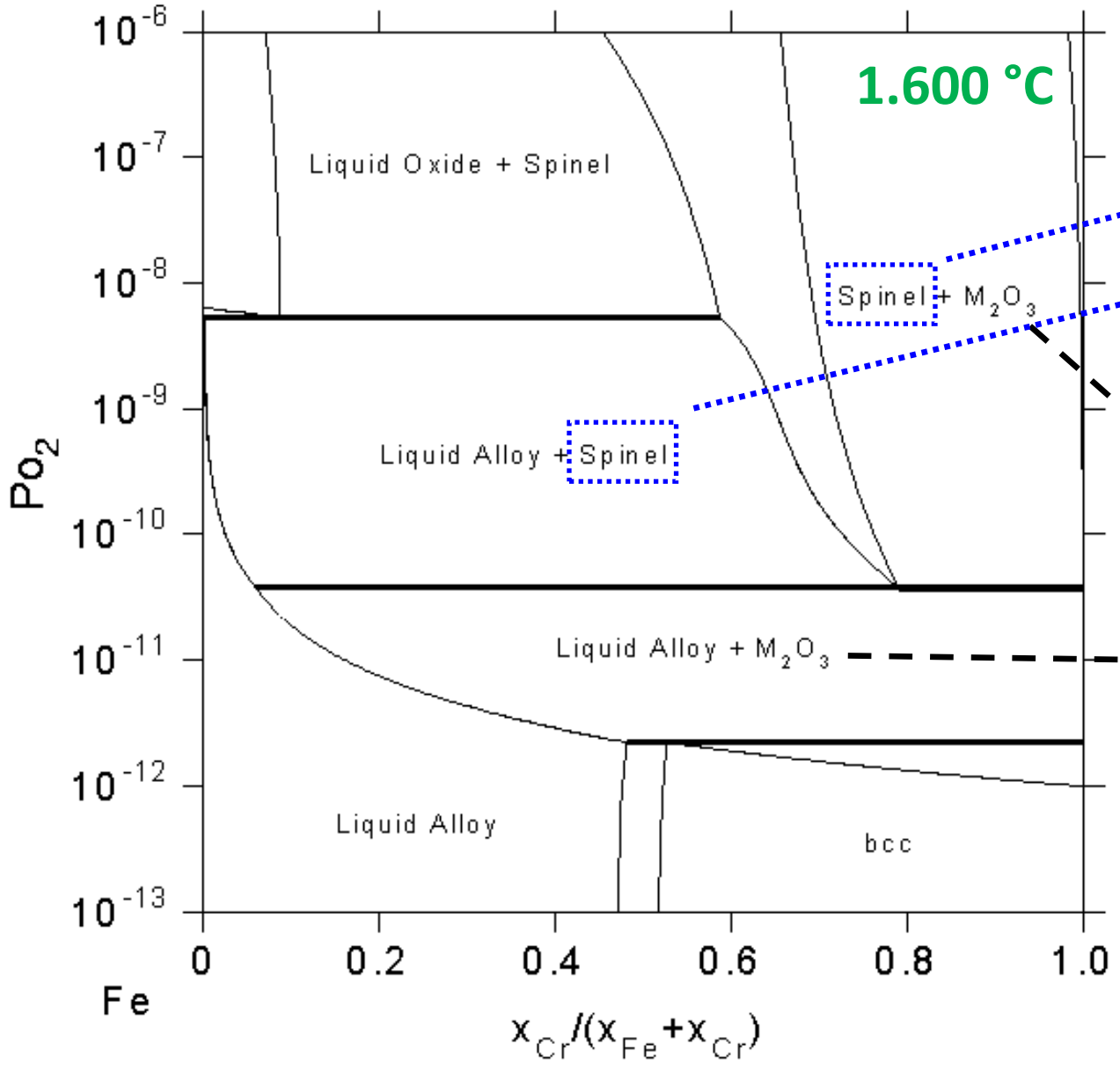


DIAGRAMA DE ESTABILIDADE DOS ESPONÉLIOS DE Cr-Fe-O (em 1.600 °C)

Óxidos de Fe (wst) e Espinélios de Cr-Fe

Ex. MAGNETITA, CROMITA

Óxidos simples (contém apenas um metal)

Ex. MAGNETITA, hematita, cassiterita

FONTE:
http://steel.ndsl.kr/htm/Fe-Cr-O.htm

SISTEMA Cr-Fe-O

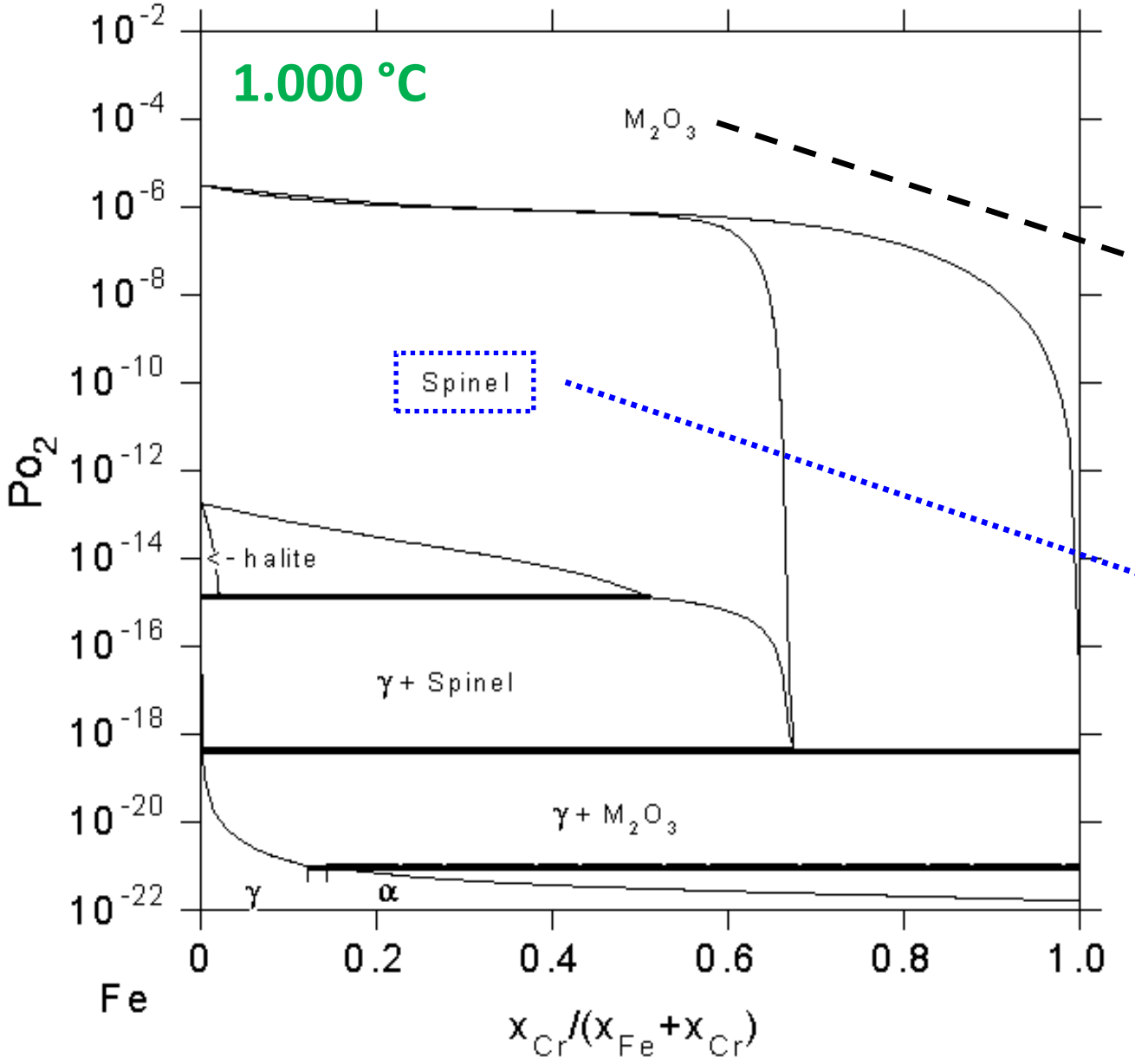


DIAGRAMA DE ESTABILIDADE DOS ESPONÉLIOS DE Cr-Fe-O

(em 1.000 °C)

Óxidos simples (contém apenas um metal)

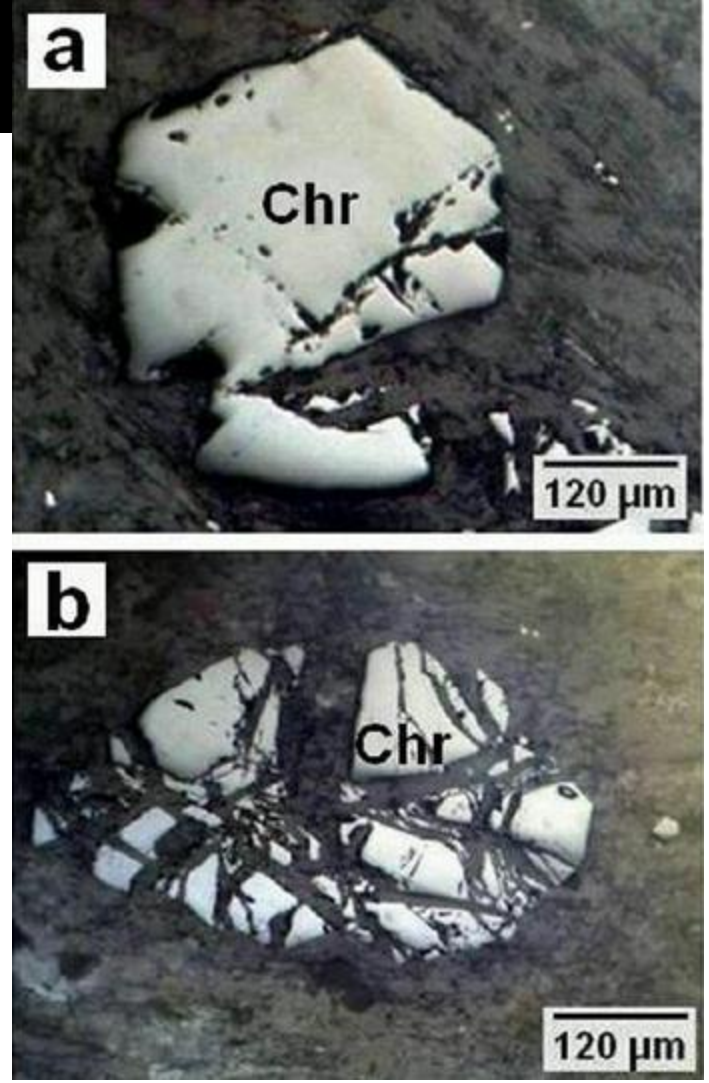
Ex. MAGNETITA, hematita, cassiterita

Óxidos de Fe (wst) e Espinélios de Cr-Fe

Ex. MAGNETITA, CROMITA

FONTE:
http://steel.ndsl.kr/htm/Fe-Cr-O.htm

CROMITA $Fe^{2+}Cr_2O_4$



▲ FONTE:
https://www.jmau.org/viewimage.asp?img=JMicroscUltrastruct_2014_2_1_41_224207_f2.jpg

COR
Cinza esbranquiçado, com tons amarronzados (pouco diagnostica).

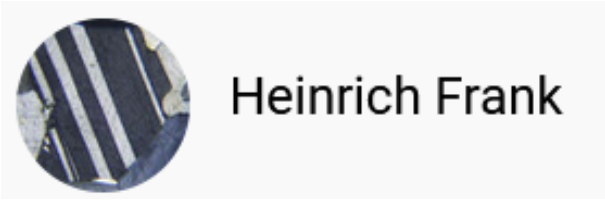
REFLECTÂNCIA
Baixa (~11%).

BIRREFLECTÂNCIA
Ausente

ANISOTROPIA
Isotrópica

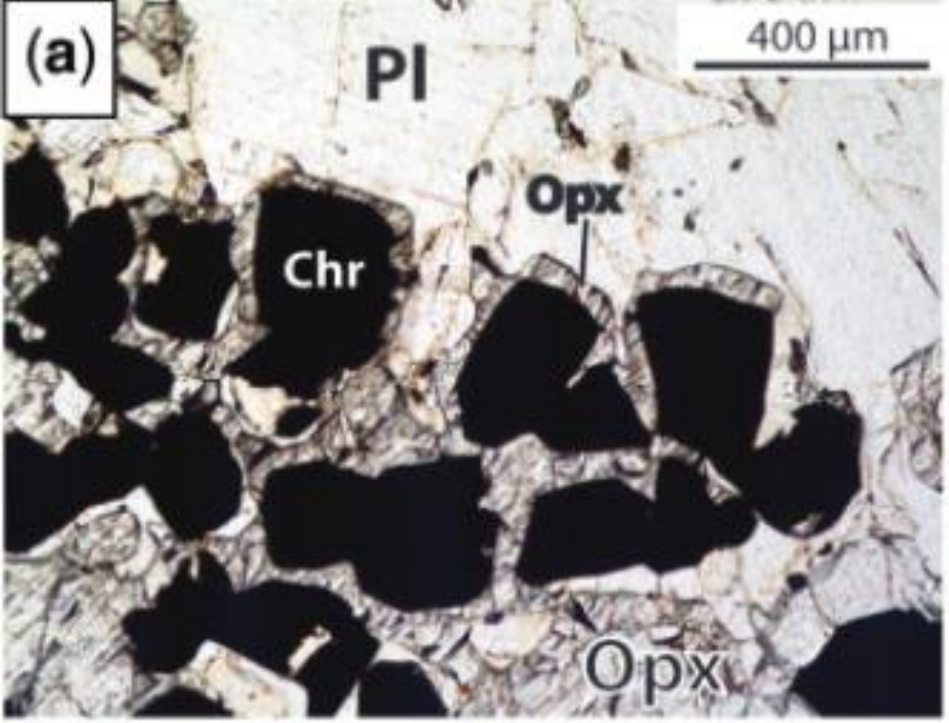
REFLEXÕES INTERNAS
Ausente a raramente vermelho-amarronzada.

Difícil reconhecimento. As paragêneses são mais úteis em sua identificação.



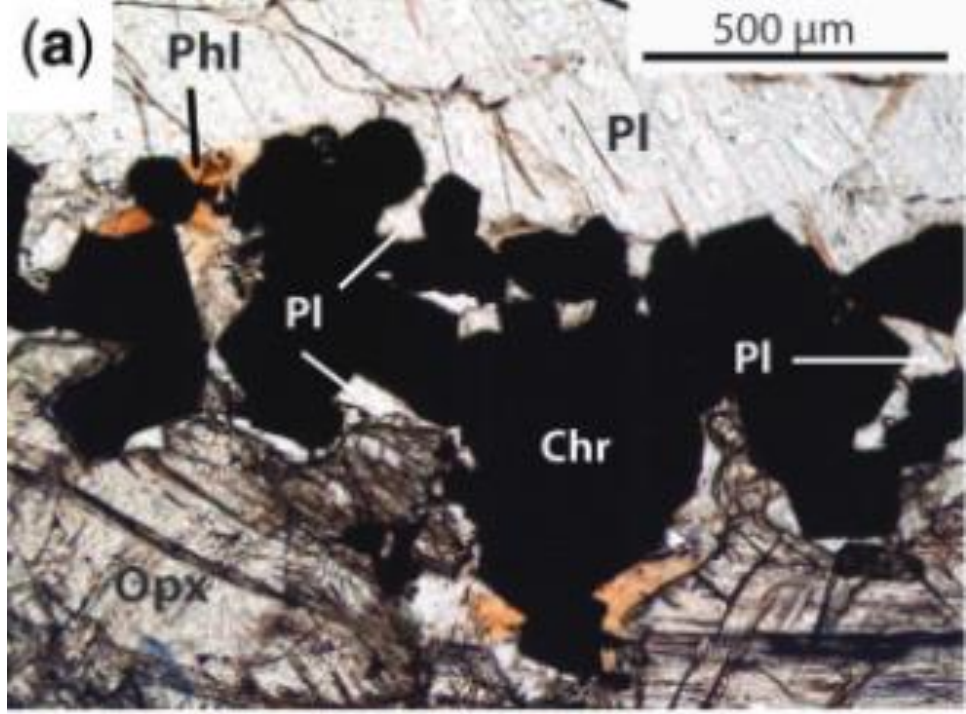
CROMITA - LUZ REFLETIDA
(POLARIZADORES DESCRUZADOS E CRUZADOS)

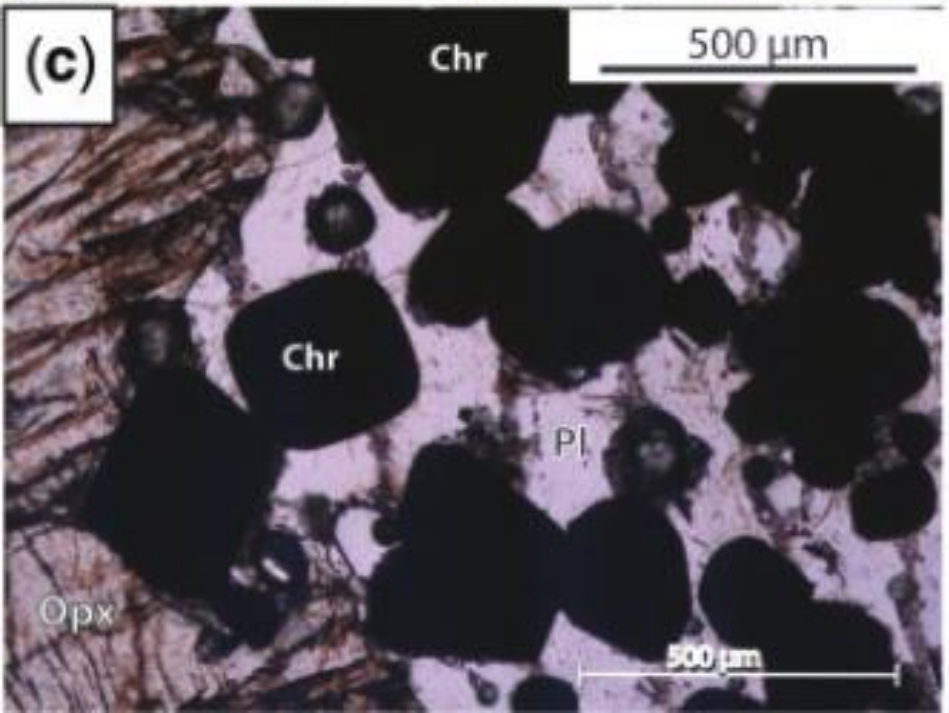
https://www.youtube.com/watch?v=2a4JhCTANrk&list=PL5k_2NCH5I4BSbSACEaq9Dfxmd3kRWf90&index=3



(a) The stringer is composed of subhedral, partially annealedgrains of Cr-spinel (Chr) with small, anhedral grains of plagioclase (Pl) and phlogopite (Phl), the latter attached to the Cr-spinel. Thestringer is underlain by feldspathic orthopyroxenite (orthopyroxene: Opx) and overlain by anorthosite. (b, c) The anorthosite juxta-posed with the stringer includes small, anhedral grains of orthopyroxene with coronas of clinopyroxene (Cpx).

►►►

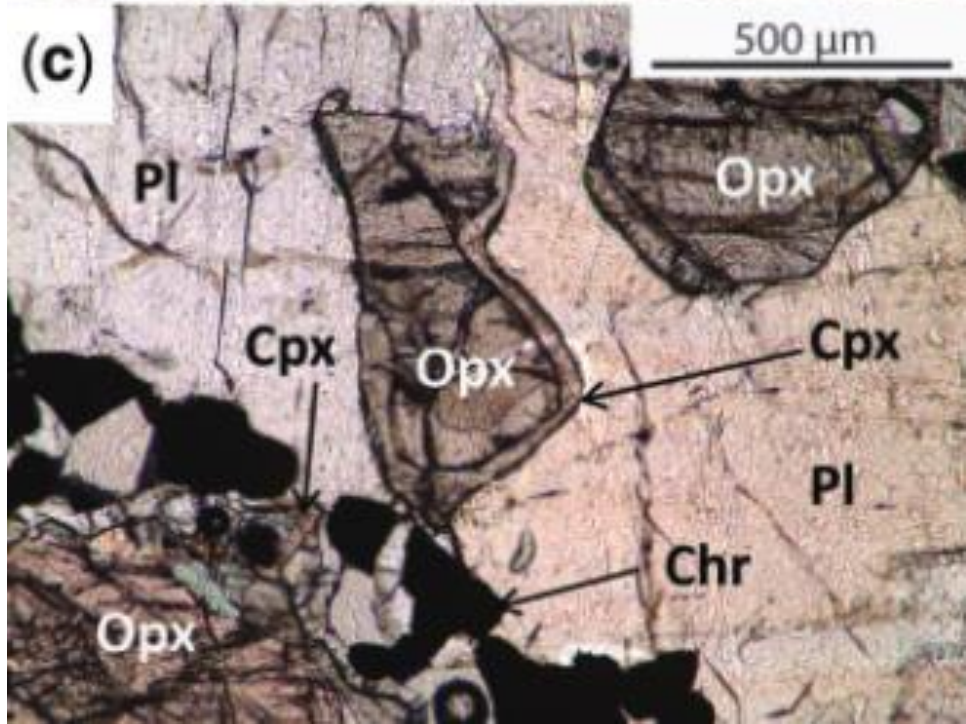




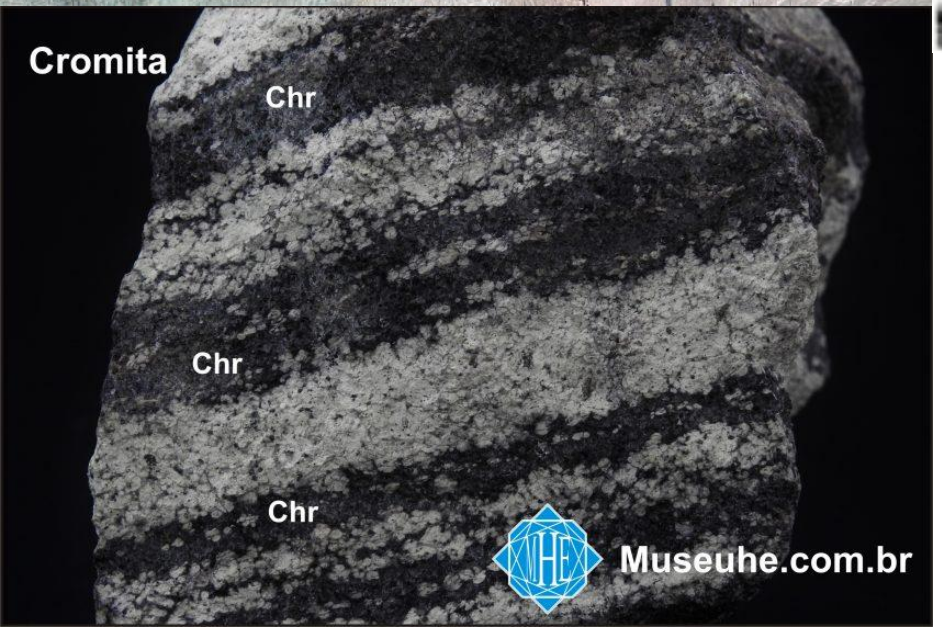
◄◄◄ (a) Photomicrograph of the MFCR Stringer (transmitted light) shows that the loosely packed grains of Cr-spinel are associ-ated with orthopyroxene (Opx) in the lower part and plagioclase (Pl) in the upper part. Overgrowths of orthopyroxene occur onsome of the grains of Cr-spinel. (b) Photomicrograph of the anorthosite above the MFCR Stringer (transmitted light) shows the oc-currence of anhedral grains of orthopyroxene together with small anhedral grains of plagioclase.

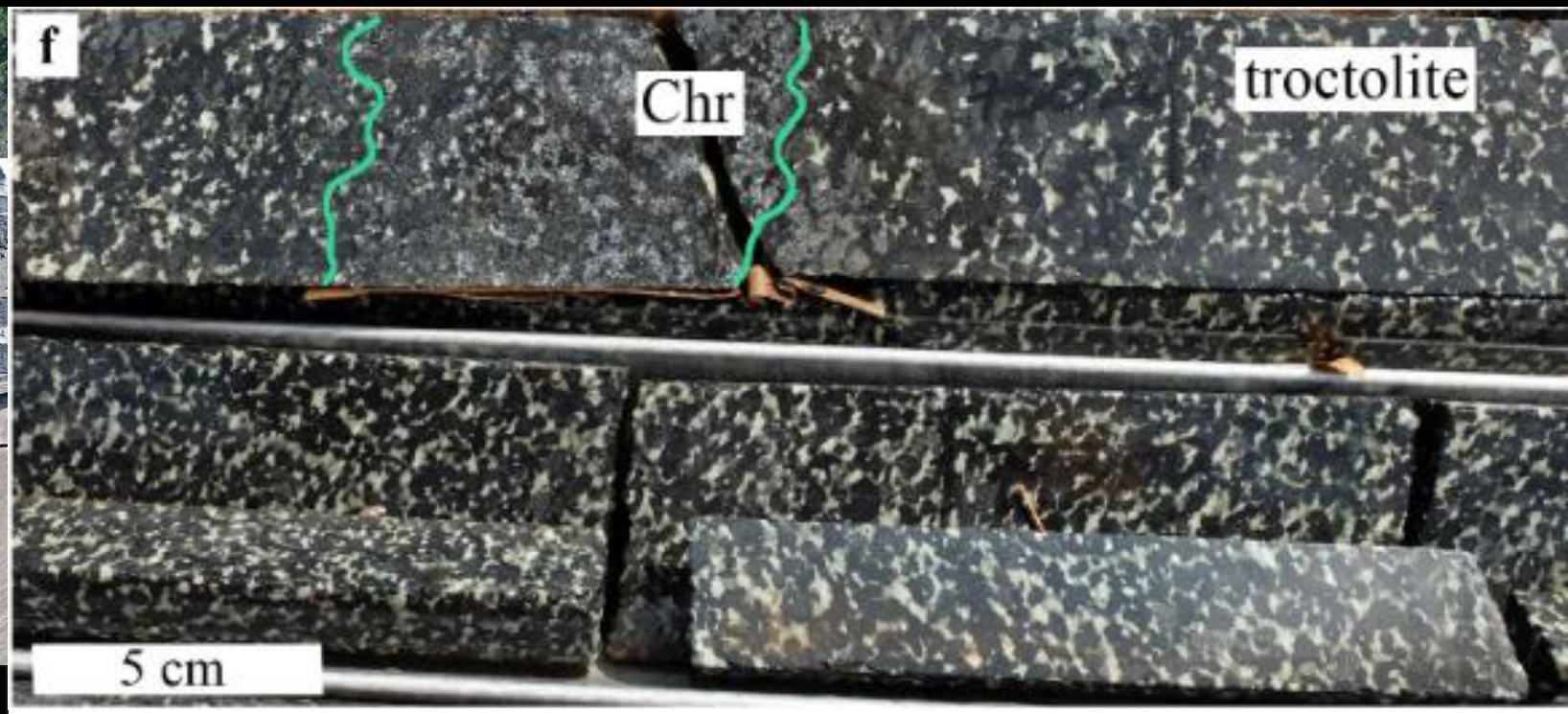
FONTE:

Scoon & Costin (2018)



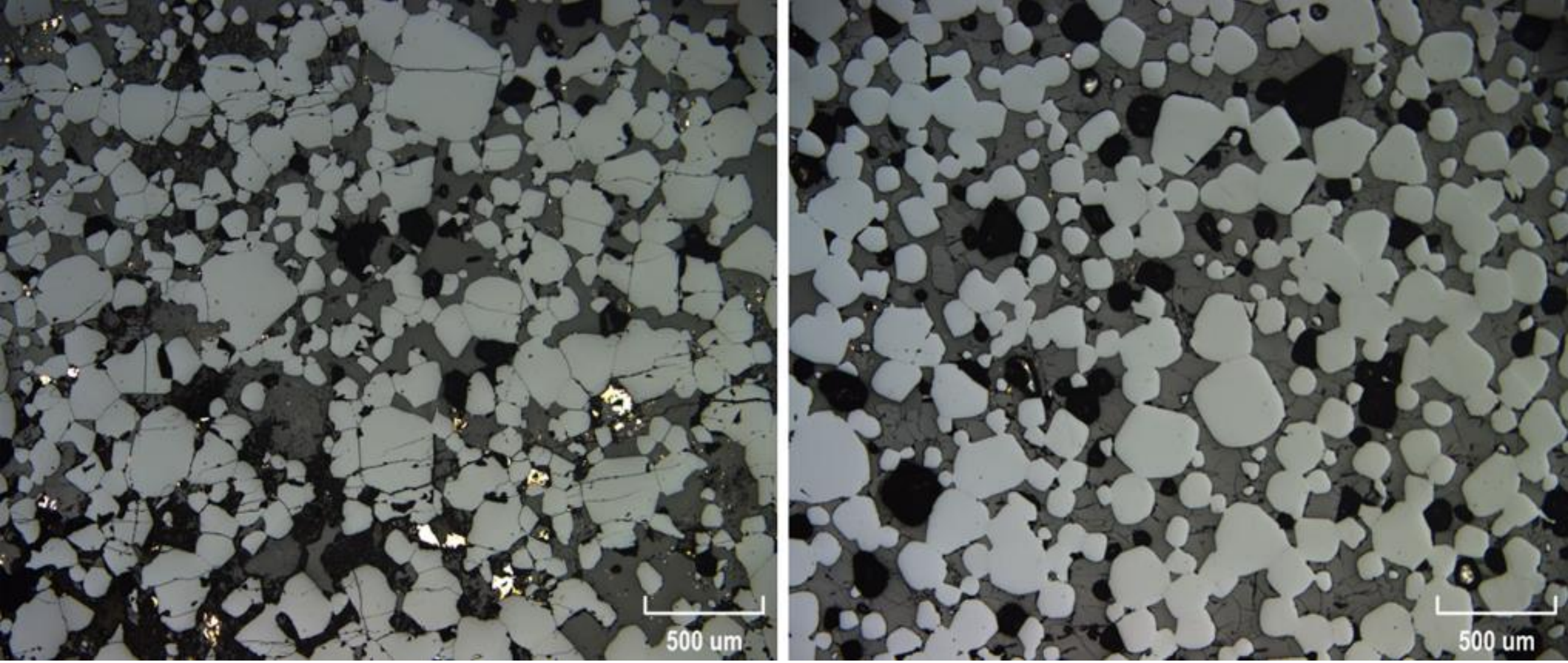
VARIAÇÕES TEXTURAIS ⟶ *CROMITA Estratiforme*





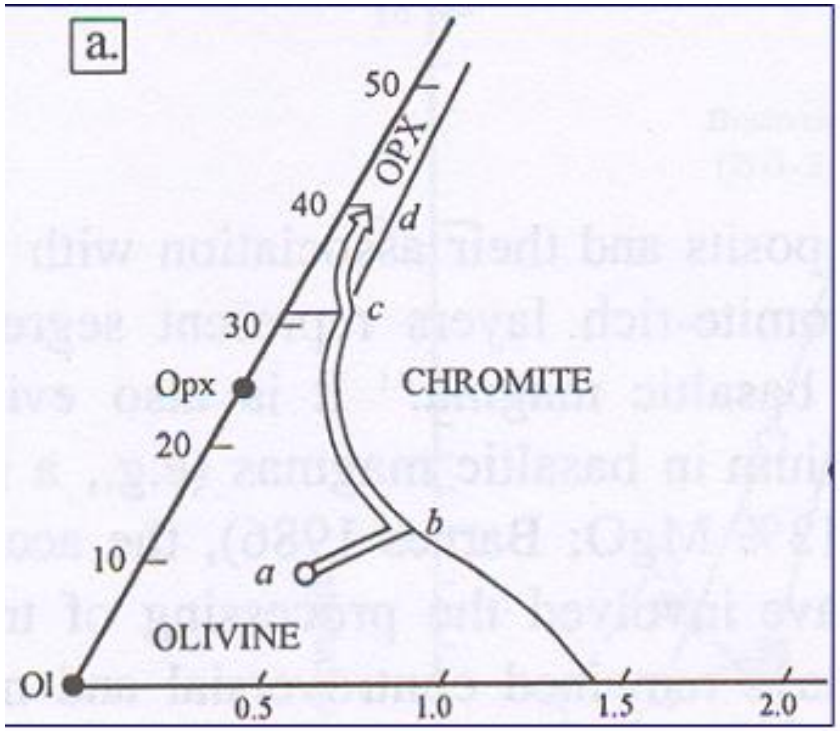
▲A disseminated chromite seam in a harzburgitic band within Waterberg troctolite (Yudovskaya et al., 2019).

Depósitos de cromita estratiforme estão geneticamente relacionados a magmas ultramáficos alojados em crosta continental estável (zonas cratônicas).

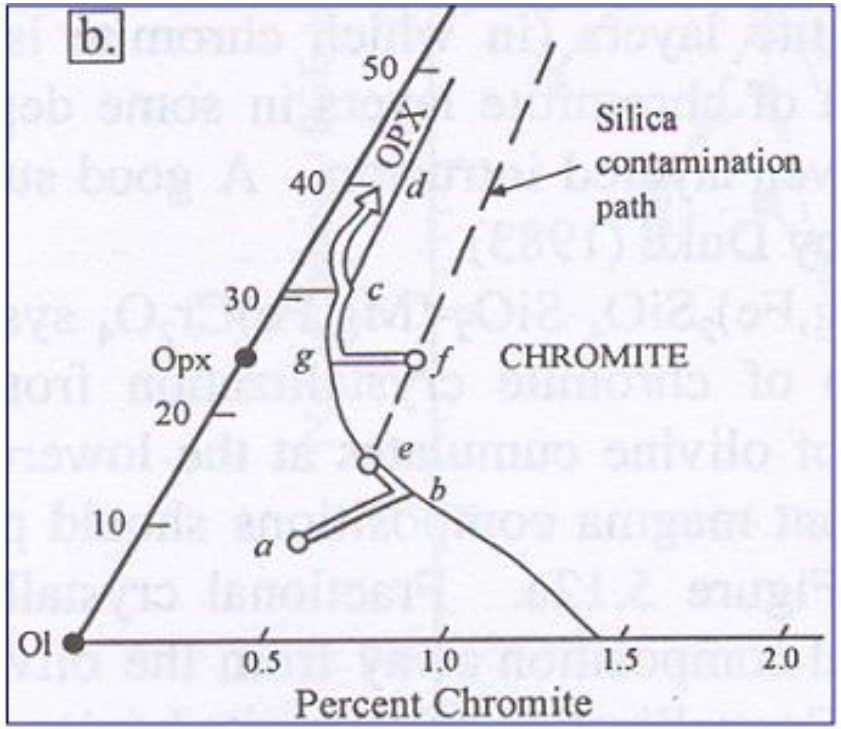


Massive portion of UG-2E chromitite; thin sectionshowing some preferential clustering of larger chromite grains to smallerchromite. Chromite occupies approximately 95% of section (light grayminerals), and sulfides occupy 1% of section (bright anhedral minerals inmatrix), whereas silicate minerals take up 4% of section (dark gray minerals making up matrix). Euhedral to subhedral to chromite grains,with grain sizes ranging from 0.04 to 0.7 mm wide.bUG-2 chromitegrains occupy 92% of section, tiny speckles of sulfide occupy 0.5%,whereas interstitial silicate minerals take up approximately 7.5%.Chromite grain sizes range from 0.01 to 0.25 mm. Lighter gray due todifferent brightness adjustment (Langa et al., 2019).

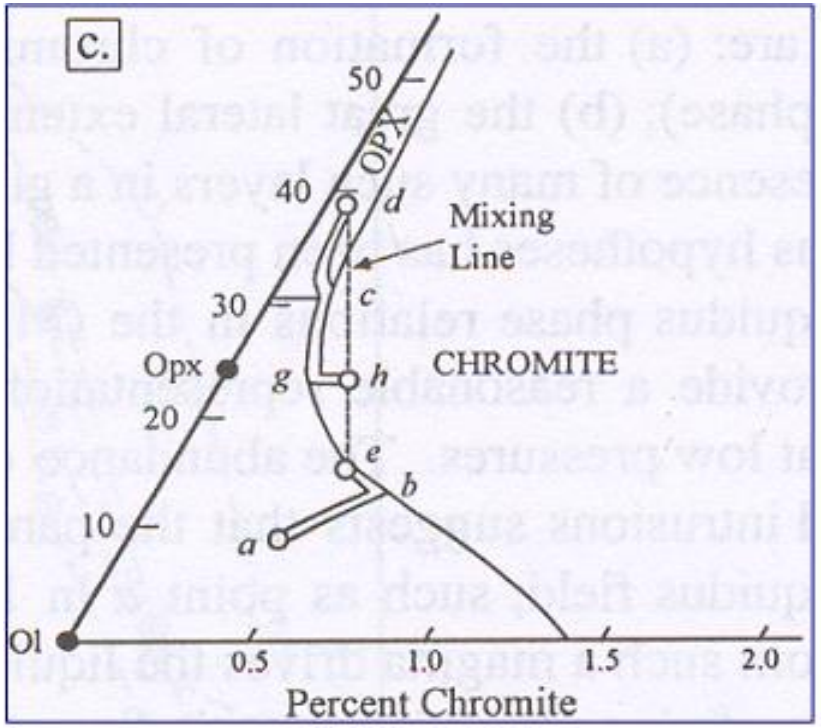
Geração de cromita em depósitos estratiforme



Cristalização fracionada normal, sem geração de cromititos.

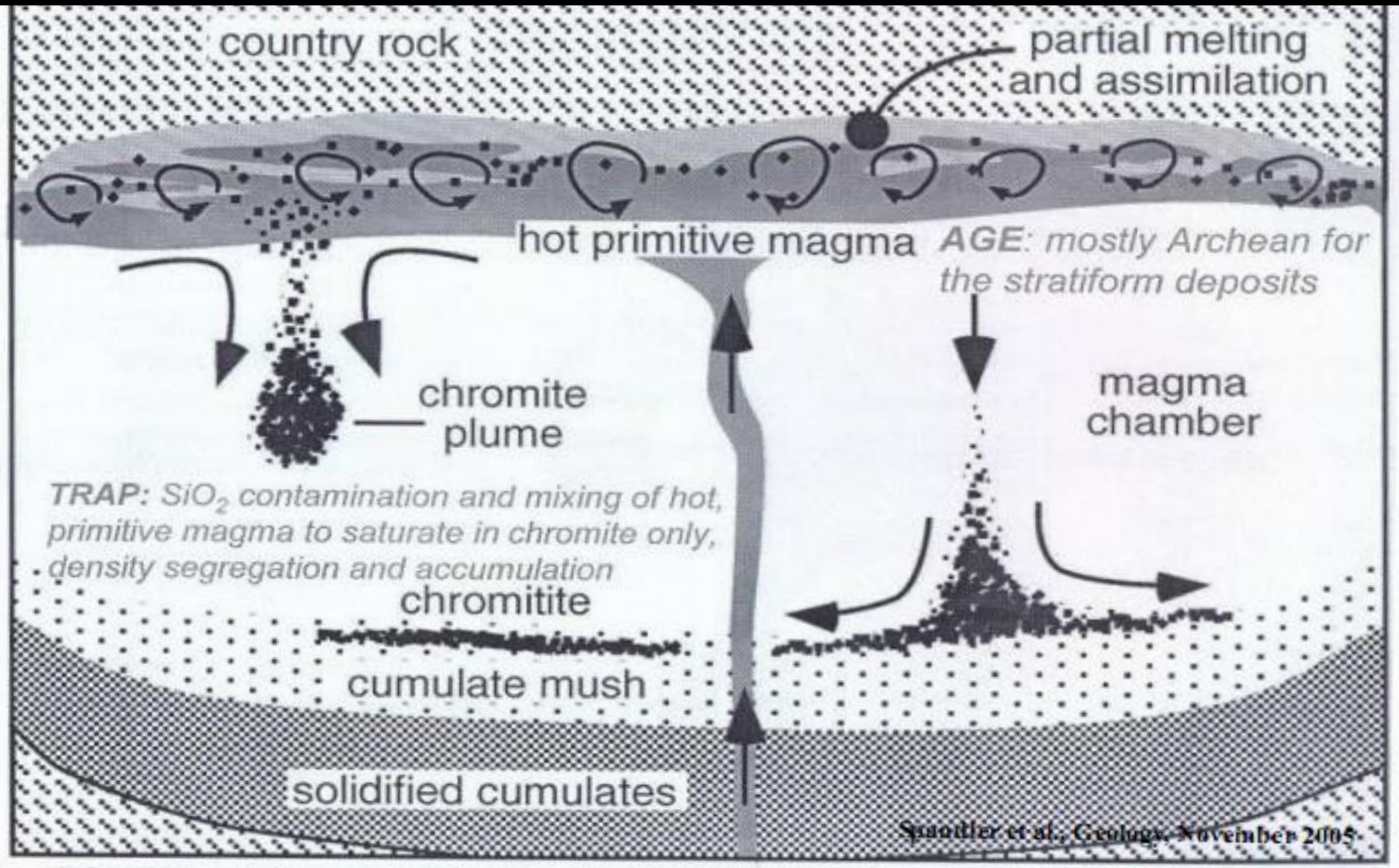


Contaminação do magma por assimilação de rochas mais ricas em sílica na crosta



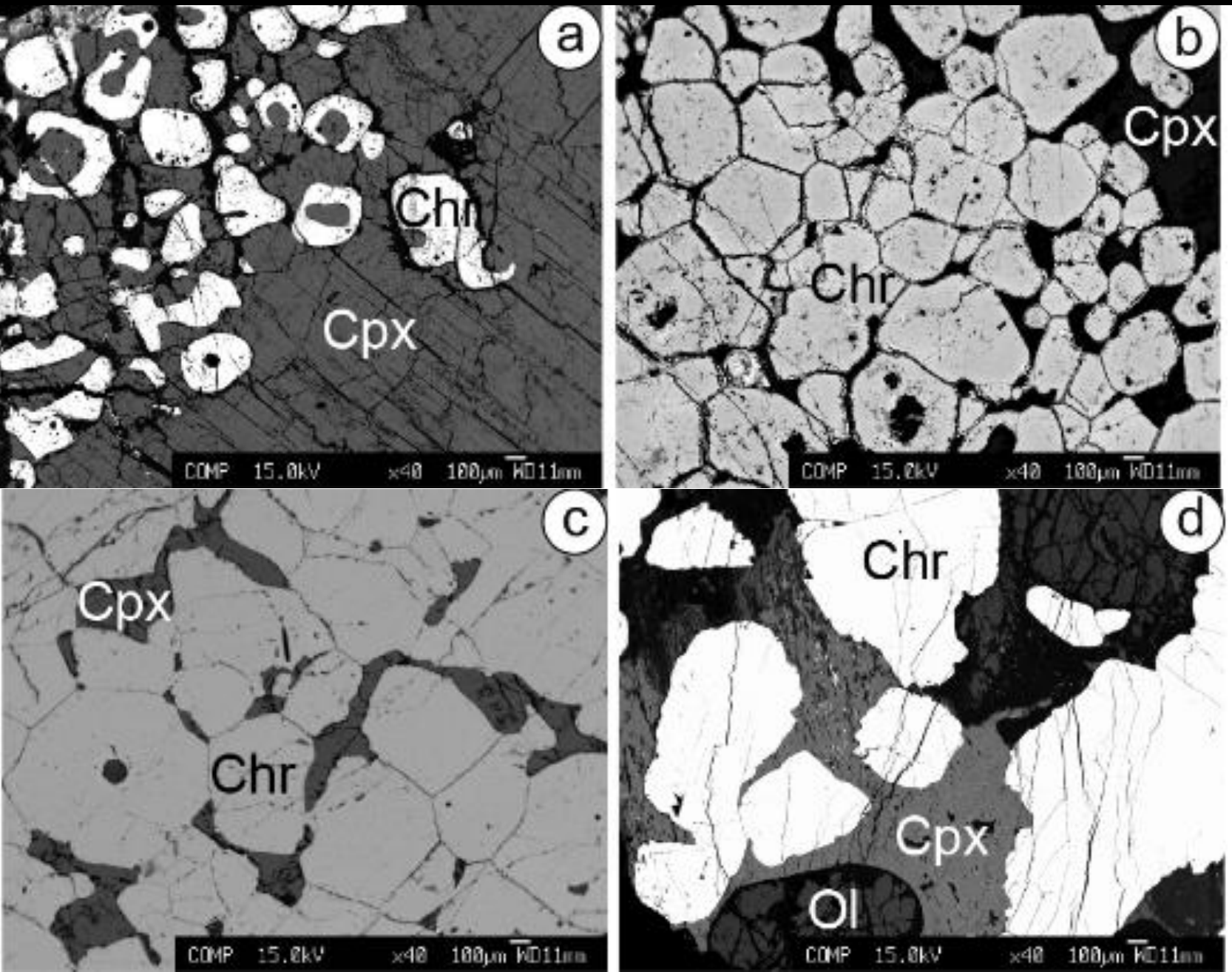
Mistura de magma primitivo com magmas enriquecidos em sílica (múltiplas intrusões)

Geração de cromita em depósitos estratiforme



SOURCE of Cr: peridotitic mantle; TRANSPORT of Cr: dissolved in magma

VARIAÇÕES TEXTURAIS ⟶ *CROMITA Estratiforme*

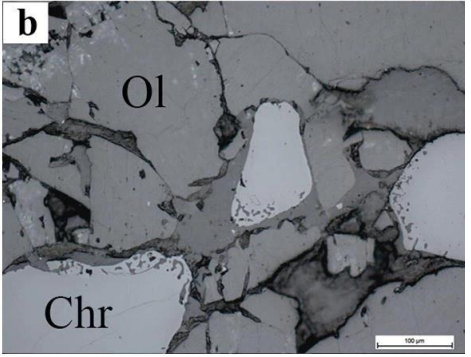


Depósitos estratiformes geram zonas de minério maciço.

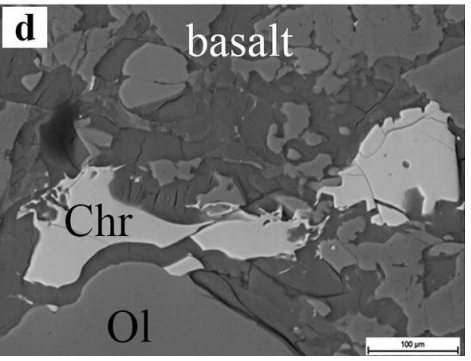
(A and B) Disseminated and massive chromitite (Cic15-10) from Kars ophiolite;
(C) Massive chromitite (PK14-02) from Pozantı-Karsantı ophiolite;
(D) Massive chromitite (KZ15-21).

Fonte:
Su et al. (2020)
https://pubs.geoscienceworld.org/msa/ammin/article-abstract/105/6/894/586739/The-occurrence-origin-and-fate-of-water-in?redirectedFrom=fulltext

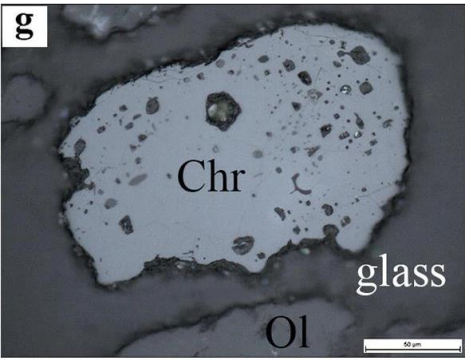
Importância da microscopia eletrônica de varredura (MEV) na petrografia e análises químicas semiquantitativas.



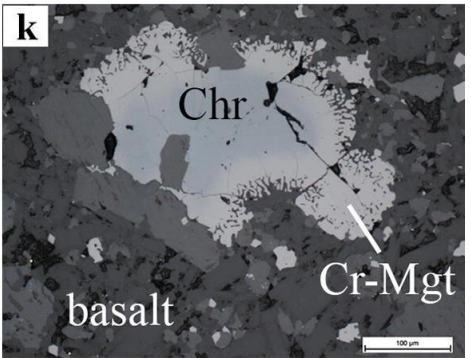
Cromita arredondada com bordas ricas em inclusões.



Cromita com textura de peneira (corroída).

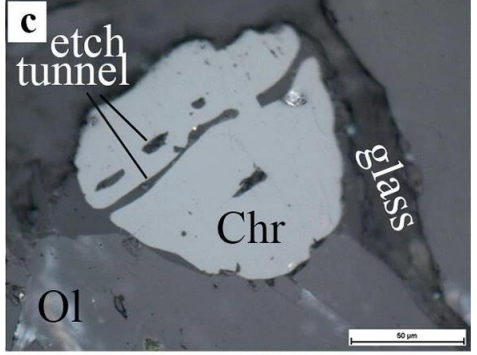


Cromita em bainha e com textura tipo peixe-anzol (*fish-hook textura*).

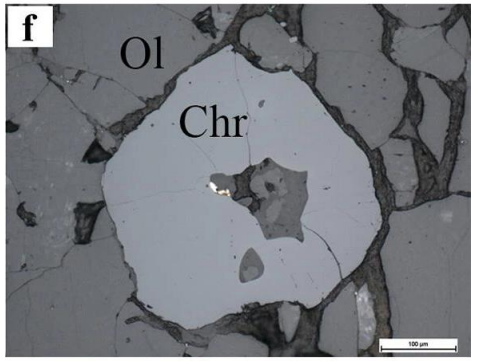


Cromita com coroa Uma corona de Cr-magnetita que exibe texutura em peneira.

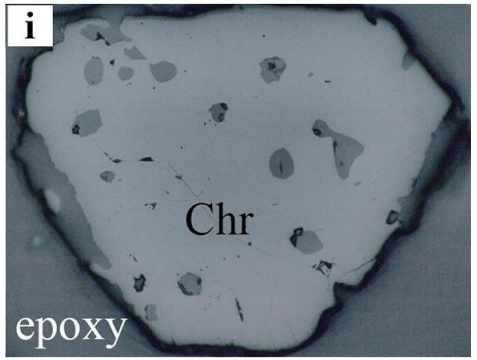
FONTE:
Yudovskaya et al. (2019)



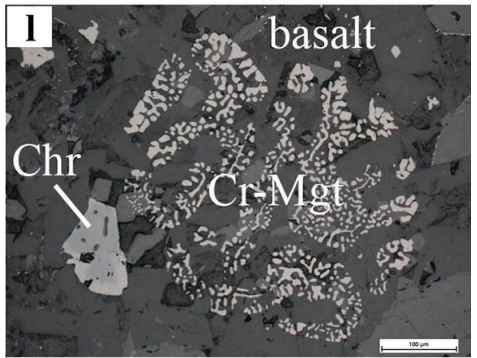
Túneis de corrosão preenchidos por vidro e trilha de inclusões em cromita.



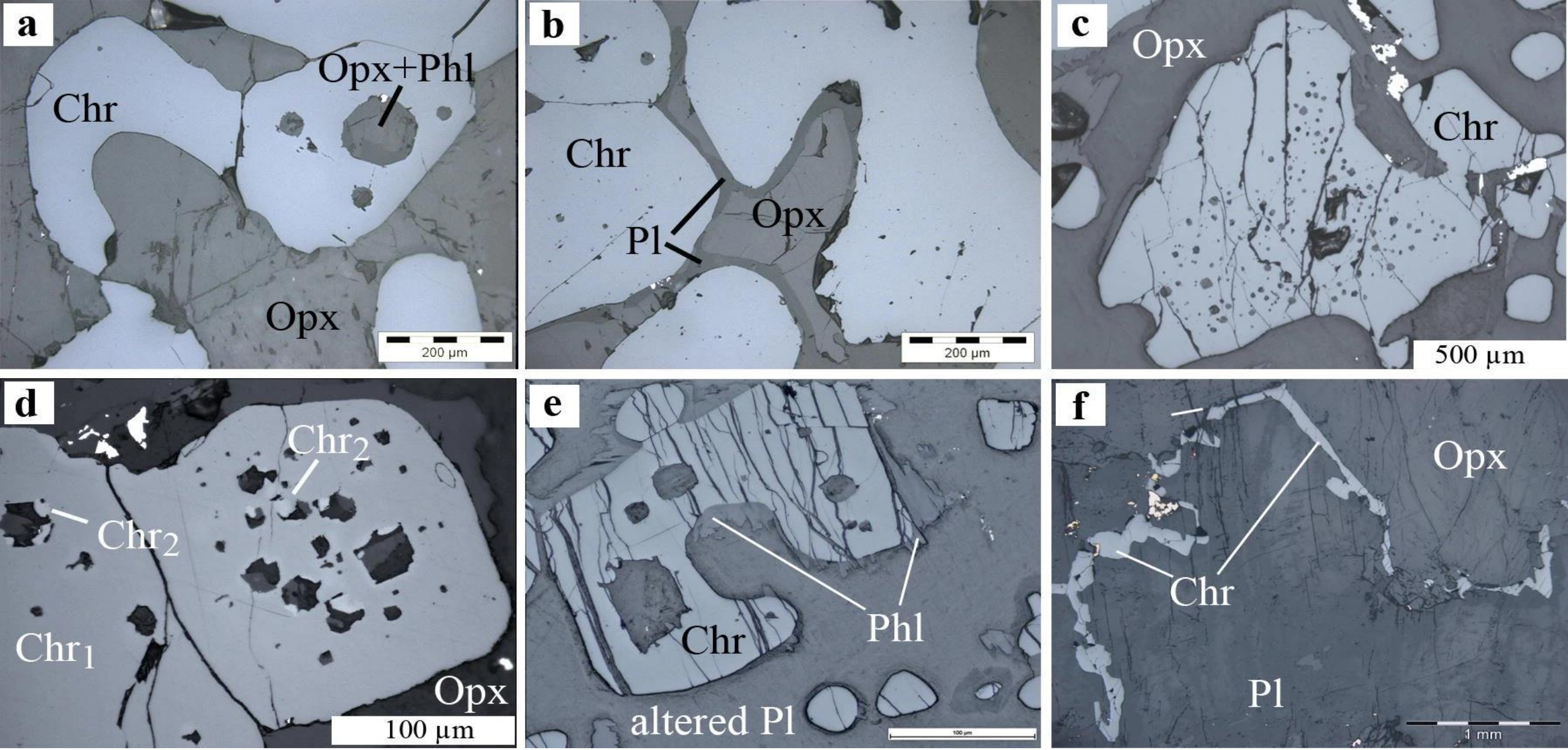
Cromita subidiomórfica com inclusões de olivina.



Inclusões de piroxênio e olivina em cromita euédrica

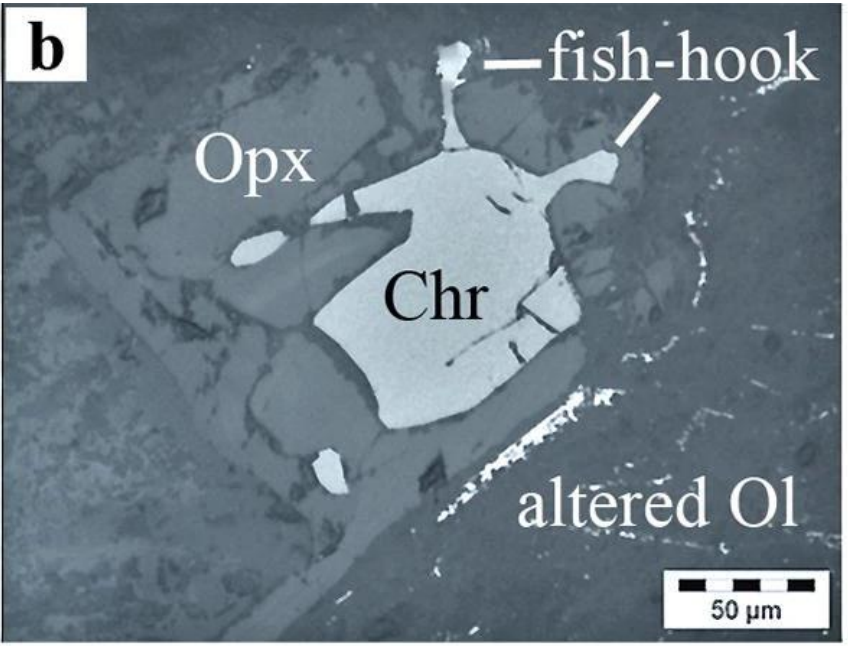


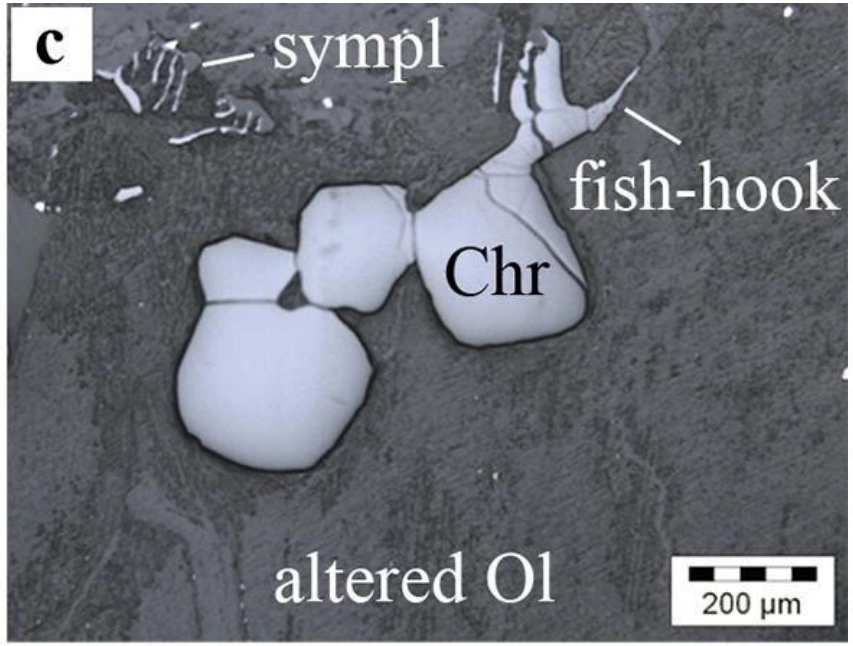
Coroa de Cr-magnetita próximo a cristal de cromita substituído pelas bordas por magnetita.

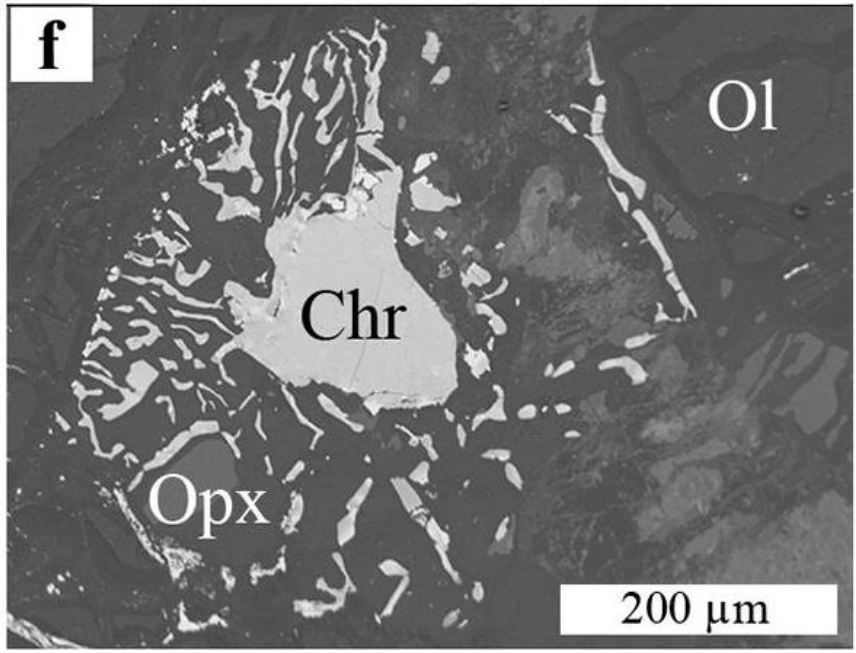


A Rounded to amoeboidal chromite with inclusions at contact between harzburgite and pyroxenite (RL, UMT314-1160). **B** Rounded chromite with plagioclase rim along with its contact with orthopyroxene, the same sample as a. **C** Sieve-textured chromite core and inclusion-free rim (RL, ATS023-289). **D** Angular inclusions in chromite with euhedral newly formed chromite (Chr2) (RL, ATS023-289). **E** Inclusions and an embayment in chromite rimmed by phlogopite (ATS23-289.2). **F** A chain of anhedral chromite along orthopyroxene-plagioclase contact (Yudovskaya et al., 2019).

VARIAÇÕES TEXTURAIS ⟶ *CROMITA Estratiforme*







B Chromite fish-hooks in orthopyroxene rim among altered olivine in troctolite (RL, WE035-613.5).

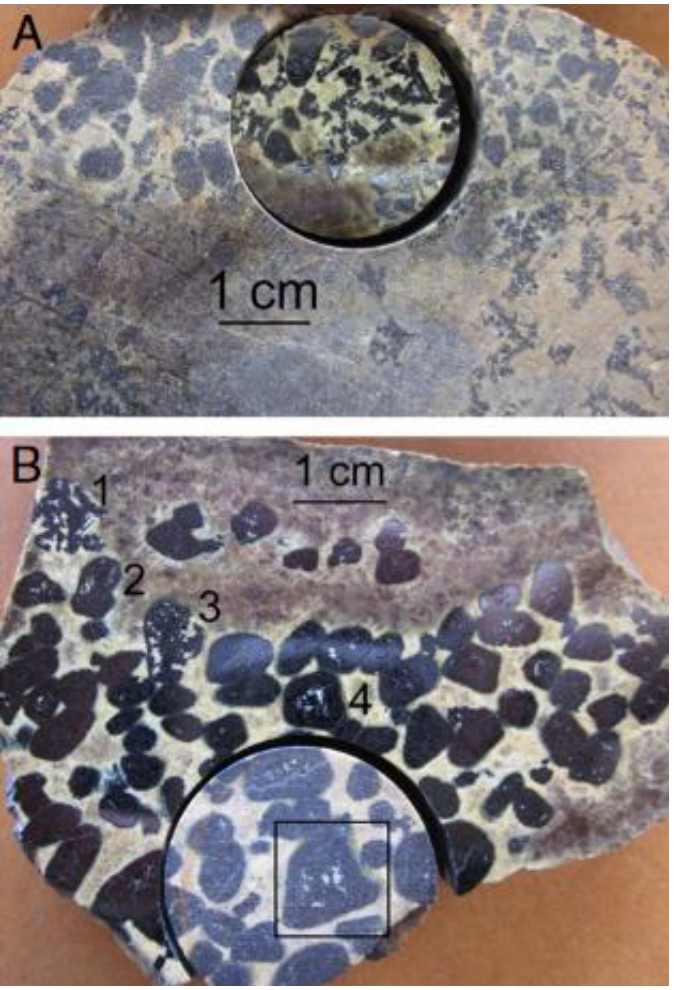
C Chromite fish-hooks transitional to symplectites in troctolite (RL, WB165-1023).

F A symplectic chromite-orthopyroxene corona around chromite.

FONTE:

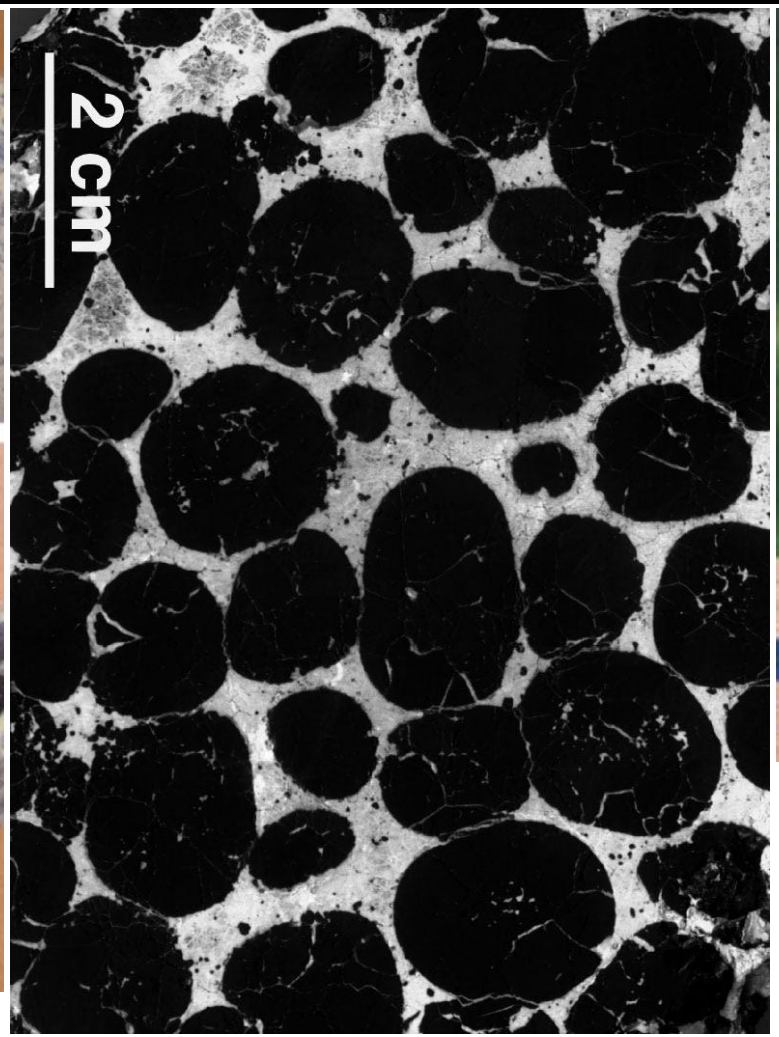
Bushveld symplectic and sieve-textured chromite is a result of coupled dissolution-reprecipitation: a comparison with xenocrystic chromite reactions in arc basalt (Yudovskaya et al., 2019).

VARIAÇÕES TEXTURAIS ⟶ *CROMITA Podiforme*



FONTE:
Prichard et al. (2015)

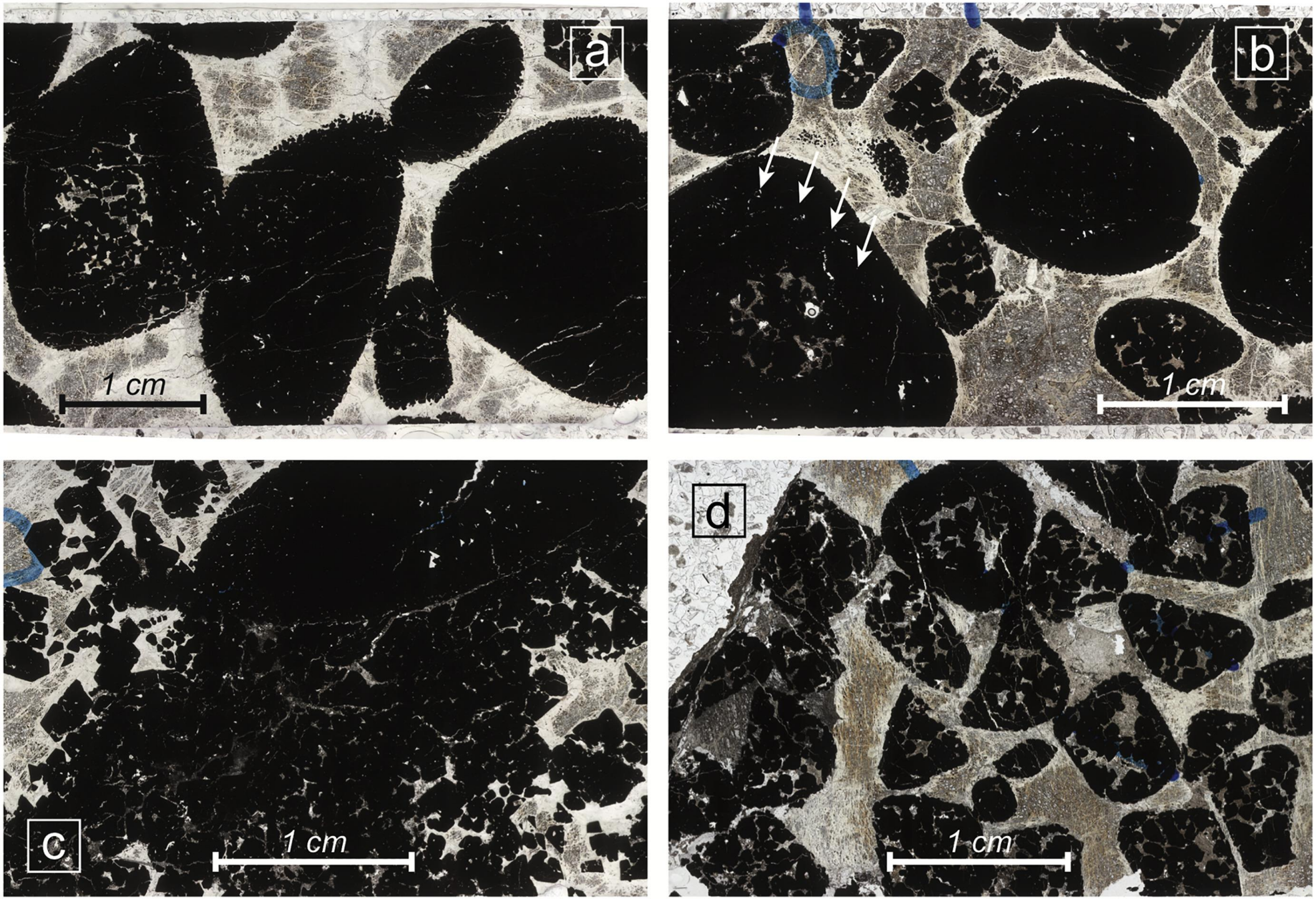
https://www.sciencedirect.com/science/article/pii/S0024493715000213?casa_token=p_YGCgxhGkUAAAAA:xzZ0fADfM4nPsMegDYGtvb9_wz6FNr1YqOJos680wTjEb9SXk1DiGC0xZZg7mL348vzdOAByhtk



Nodular podiform chromite ore from Cyprus. Dark roundish nodules of polycrystalline aggregates of magnesiochromite set in a formerly dunitic matrix, now hydrated and oxidized to chrysotile, talc, tremolite, and magnetite (Matveev & Ballhaus, 2002)

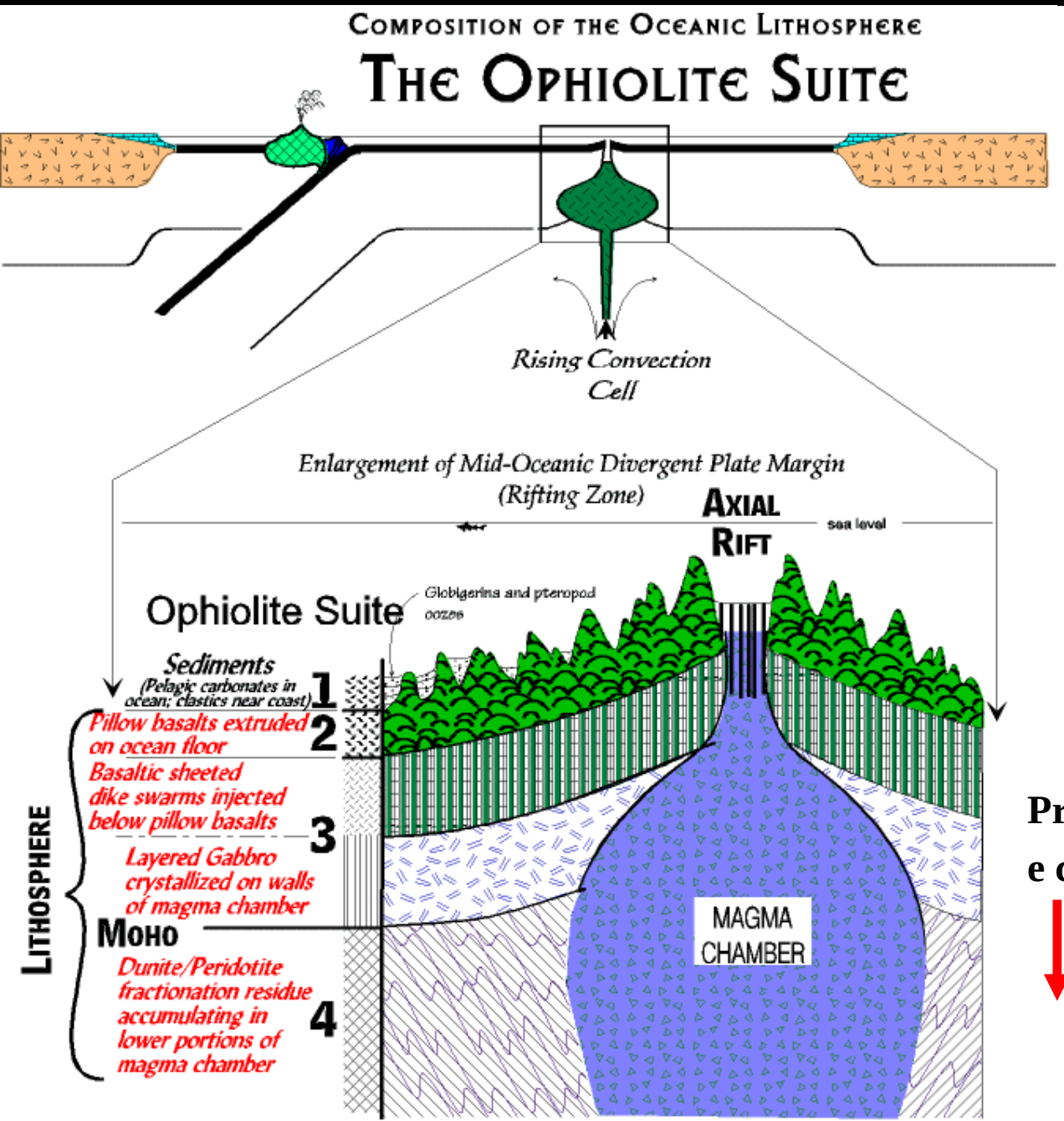
FONTE:
http://www.cyprusgeology.org/english/images/8_GF19.htm

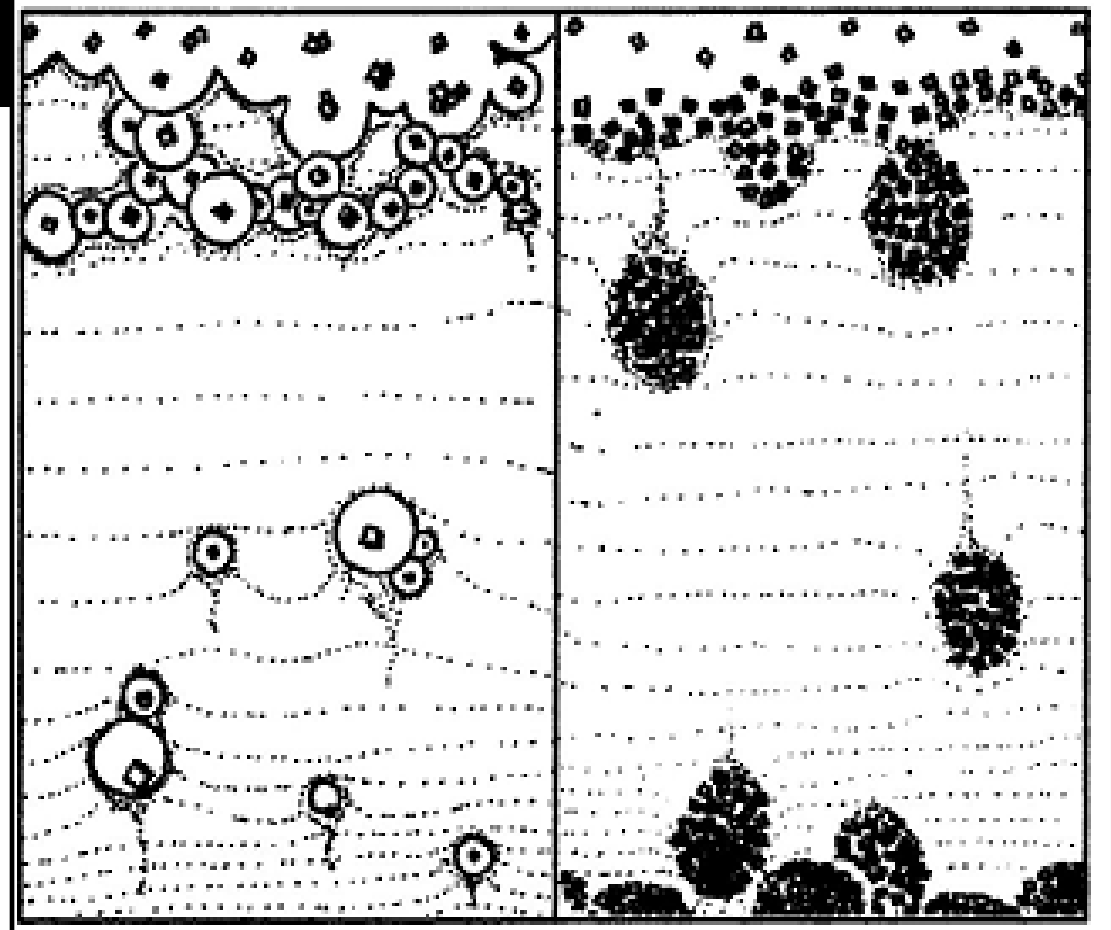
Correspondem a depósitos de cromita vinculados c complexos ofiolíticos (depósitos de crosta oceânica).



Aspect of nodules in thin section (natural light). Nodules are made of a mantle of aggregated (and partly disaggregated) minute chromite grains surrounding a nucleus of chromite and silicates (mostly olivine and plagioclase and their alteration products). The interstitial matrix between nodules is essentially serpentinized olivine. One isolated nucleus (upper right) shows evidence of skeletal growth. b) Chromite nodules with girdles of inclusions (arrows). c) Heterogeneity of size and shape of nodules. d) Nodules of small size (Zagrtdenov et al., 2018).

Geração de cromita nodular



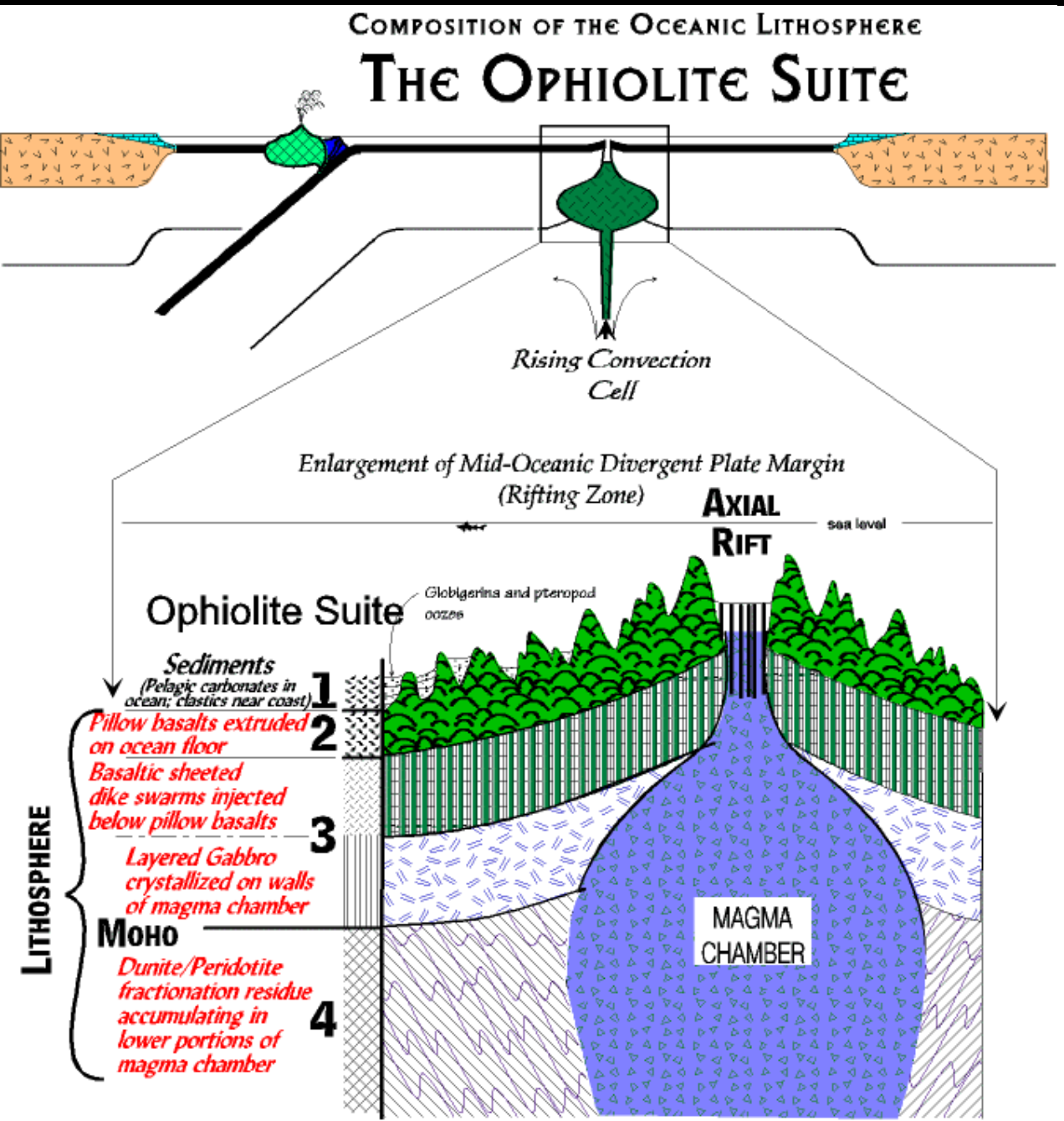


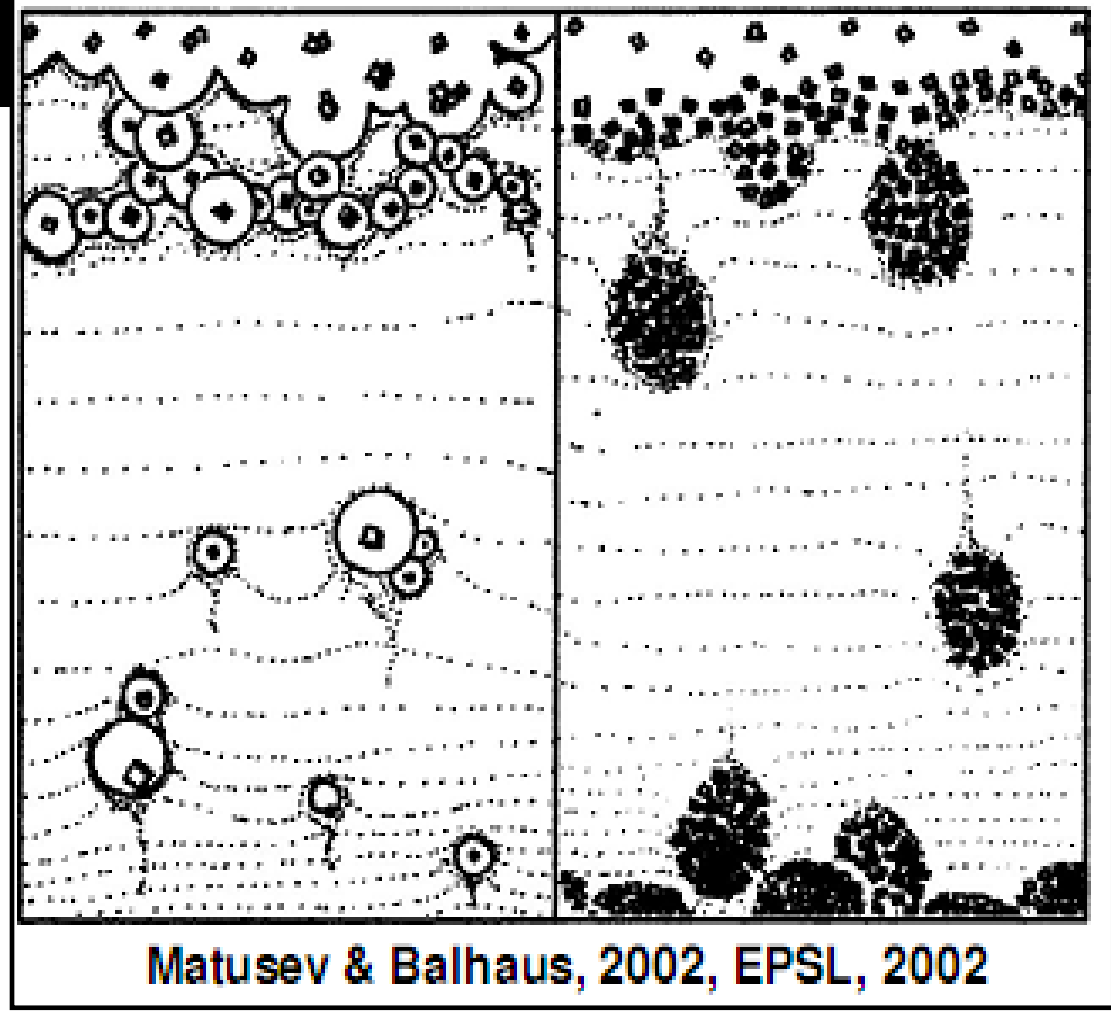
Matusev & Balhaus, 2002, EPSL, 2002

Processo de enriquecimento exige separação física entre olivina e cromita em T magmática para produzir texturas nodulares.

Fundido basáltico saturado em olivina e cromita + fase fluida aquosa → Olivina fraciona-se para fundido e fluido se adere à cromita.

Geração de cromita nodular



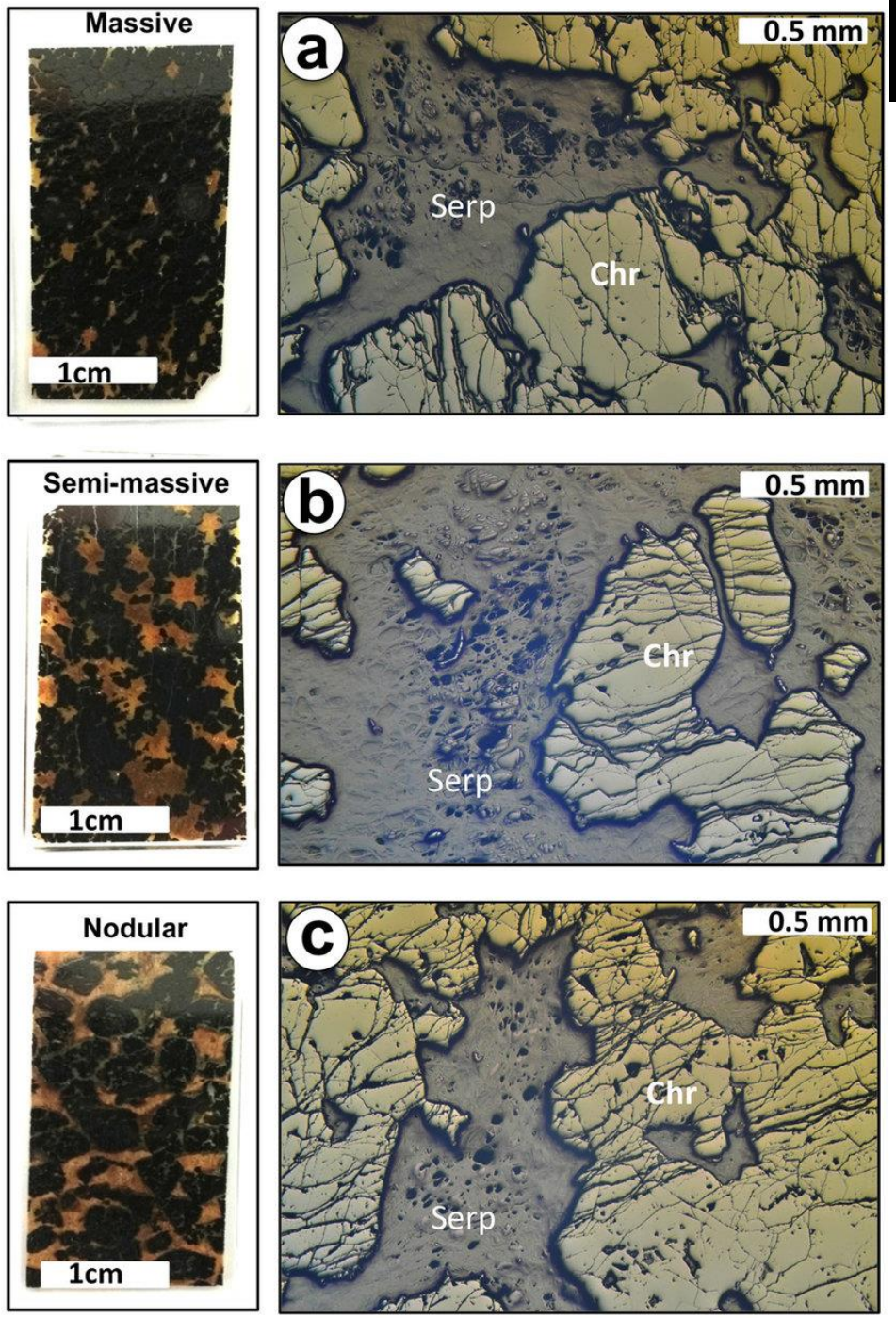


Flotação da cromita e formação de agregados

A alta densidade causa a separação dos agregados policristalinos de cromita.

VARIAÇÕES TEXTURAIS ⟶ *CROMITA Podiforme*

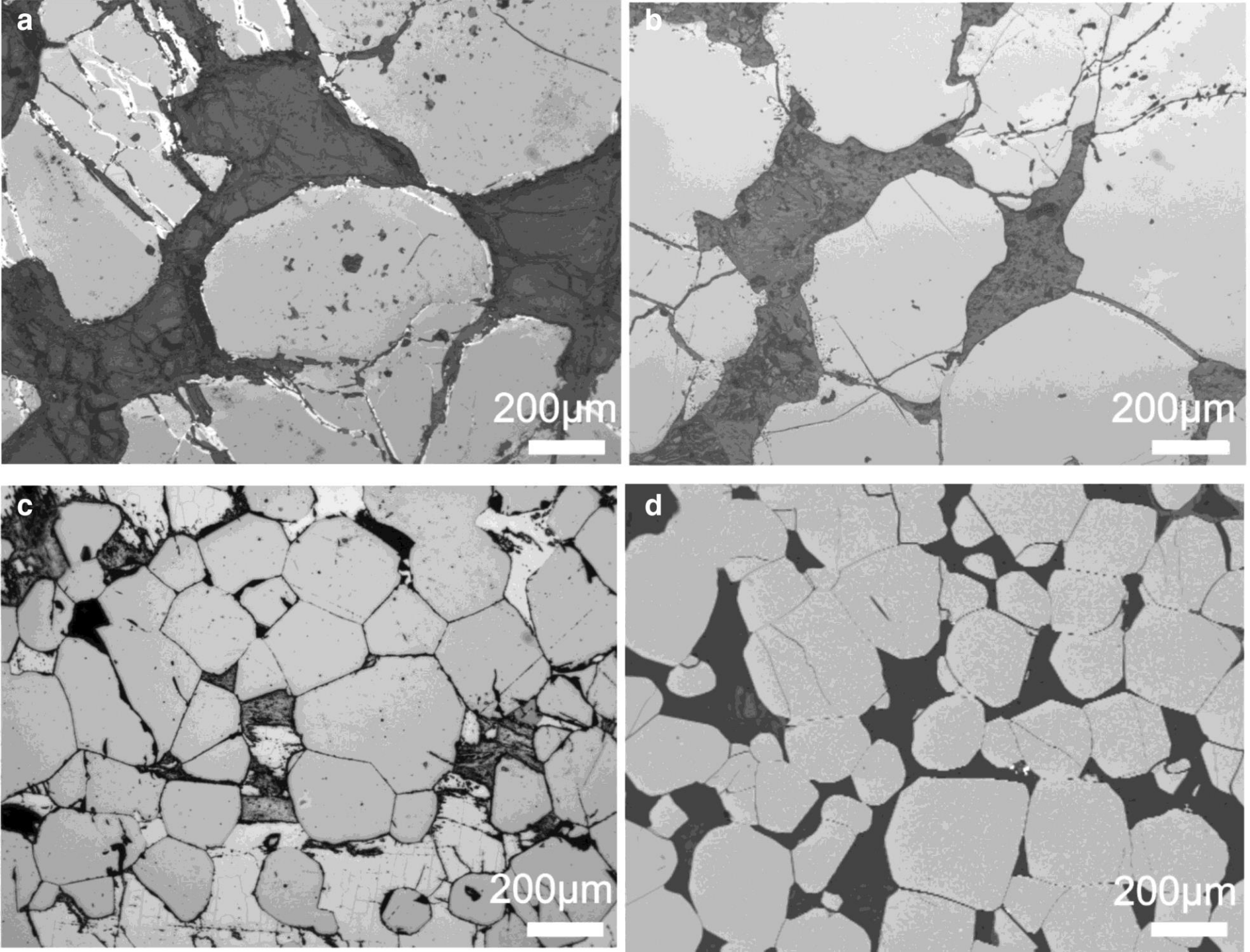
Depósitos nodulares/podiformes também podem gerar minério maciço.



Photographs of thin sections of chromitite and photomicrographs (reflected light) showing main textural types in the Cerro Colorado chromitite body:
(A) Massive chromitite;
(B) Semi-massive chromitite; and
(C) nodular chromitite.
Keys: Chr: chromite, Serp: serpentine.

FONTE:
Mendi et al. (2020)

https://www.researchgate.net/publication/340438983_Petrogenesis_of_the_chromitite_body_from_the_Cerro_Colorado_ophiolite_Paraguana_Peninsula_Venezuela



Photomicrographs illustrating the difference in shape between:

→ ophiolitic (a and b) and;

→ layered complex (c and d) chromite grains.

(a) Al 'Ays, Saudi Arabia; (b) Semail, Oman; (c) Bushveld, RSA; and (d) Stillwater, USA.

FONTE:
Prichard et al. (2018).

https://pubs.geoscienceworld.org/minmag/article/82/3/457/544742/A-mechanism-for-chromite-growth-in-ophiolite?casa_token=2DtiGapFVIMAAAAA:h4otxNHobpEqVvPtJeOr45fNX3F5UUN-BmrThgmImH63j2fh5bmQr-uc6oD0O_-ISiy2STeG

ÓXIDOS DE Sn e W

Os óxidos estão individualizados em dois grupos principais

ÓXIDOS SIMPLES

- **Contém um único metal combinado ao oxigênio**
  - **Proporção X:O**

XO

X2O

X_2O_3

(magnetita, hematita, CASSITERITA)

ÓXIDOS MÚLTIPLOS

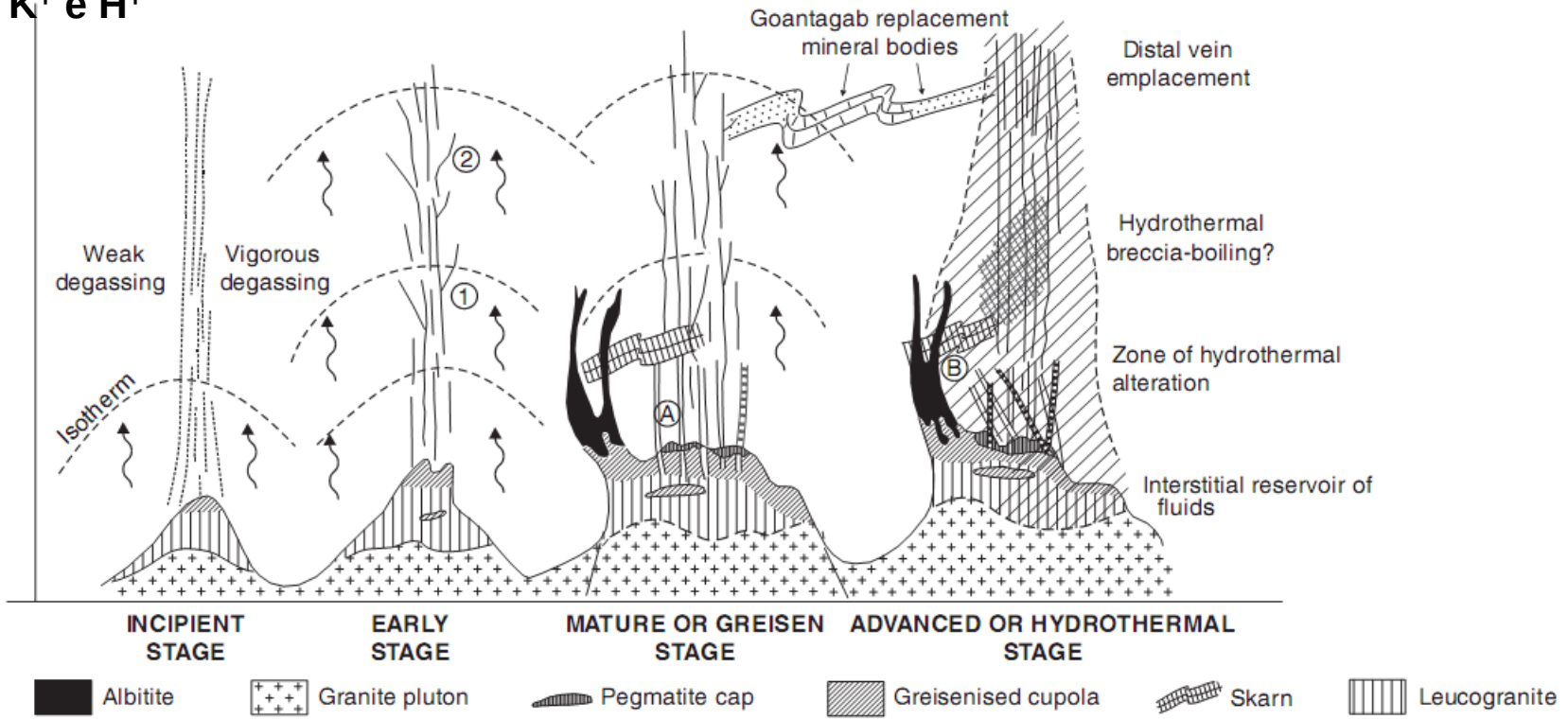
- **Contém dois metais não equivalentes (X e Y) ligados ao oxigênio**

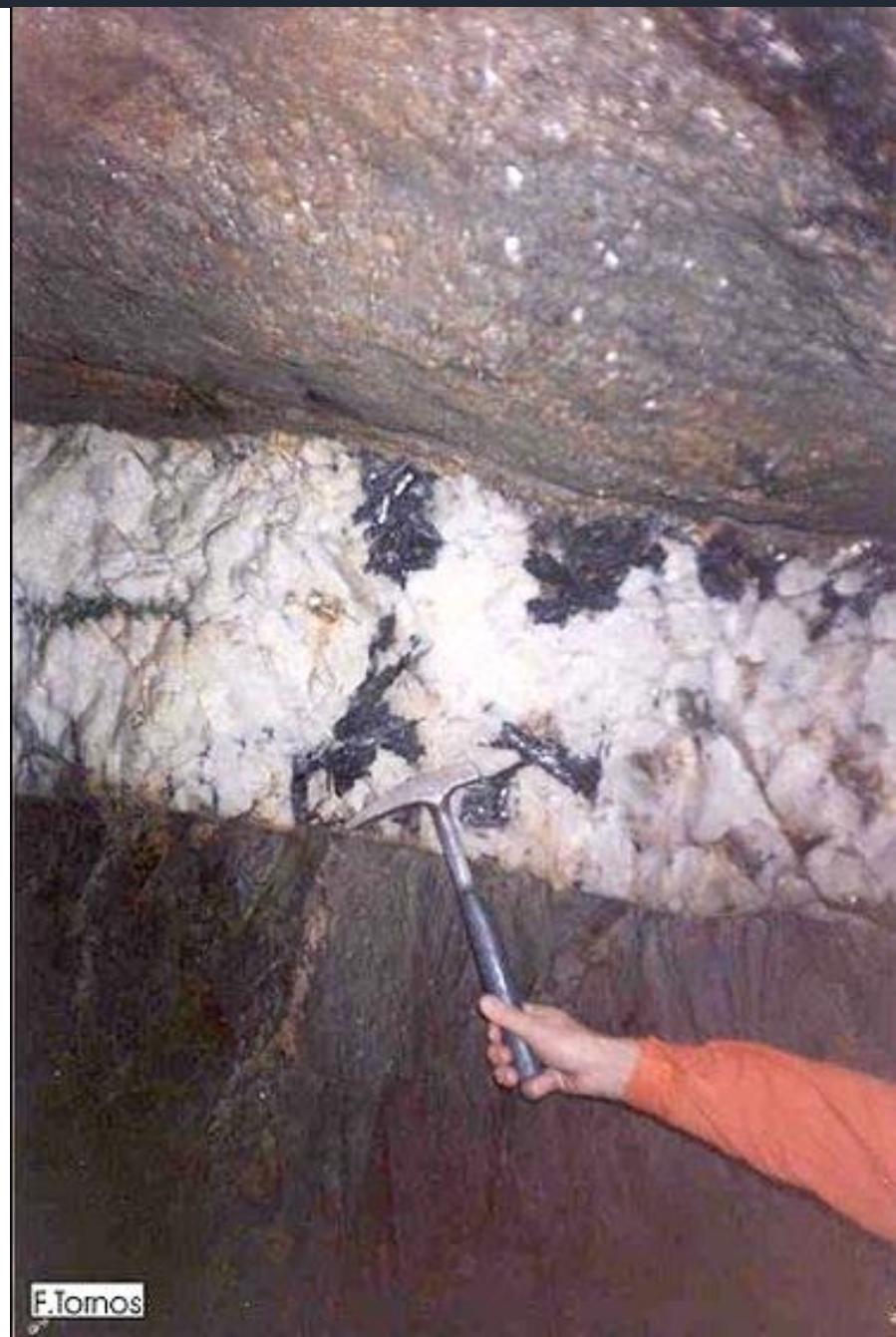
Relação XY_2O_4

(cromita, SCHEELITA, WOLFRAMITA, tungstato de ferro, tungstato de manganês)

ÓXIDOS DE Sn e W → Greisens Sn-W

- Magmas hidratados (>8% H_2O) *granitóides duas micas (Mus + Bt).*
- Cristalização a grandes profundidades (3 até 10km)
- Sistemas "fechados"
- Concentração de fase aquosa + volátil na cúpula da intrusão
- Solução hidrotermal
- Soluções ricas em voláteis derivadas de processo pós-magmático → *endogreisen*
- Formação de porosidade secundária (fraturas, brechas) → *exogreisen*
- Aumento da concentração de voláteis, F, B, Li e aumento da atividade do Na^+, K^+ e H^+



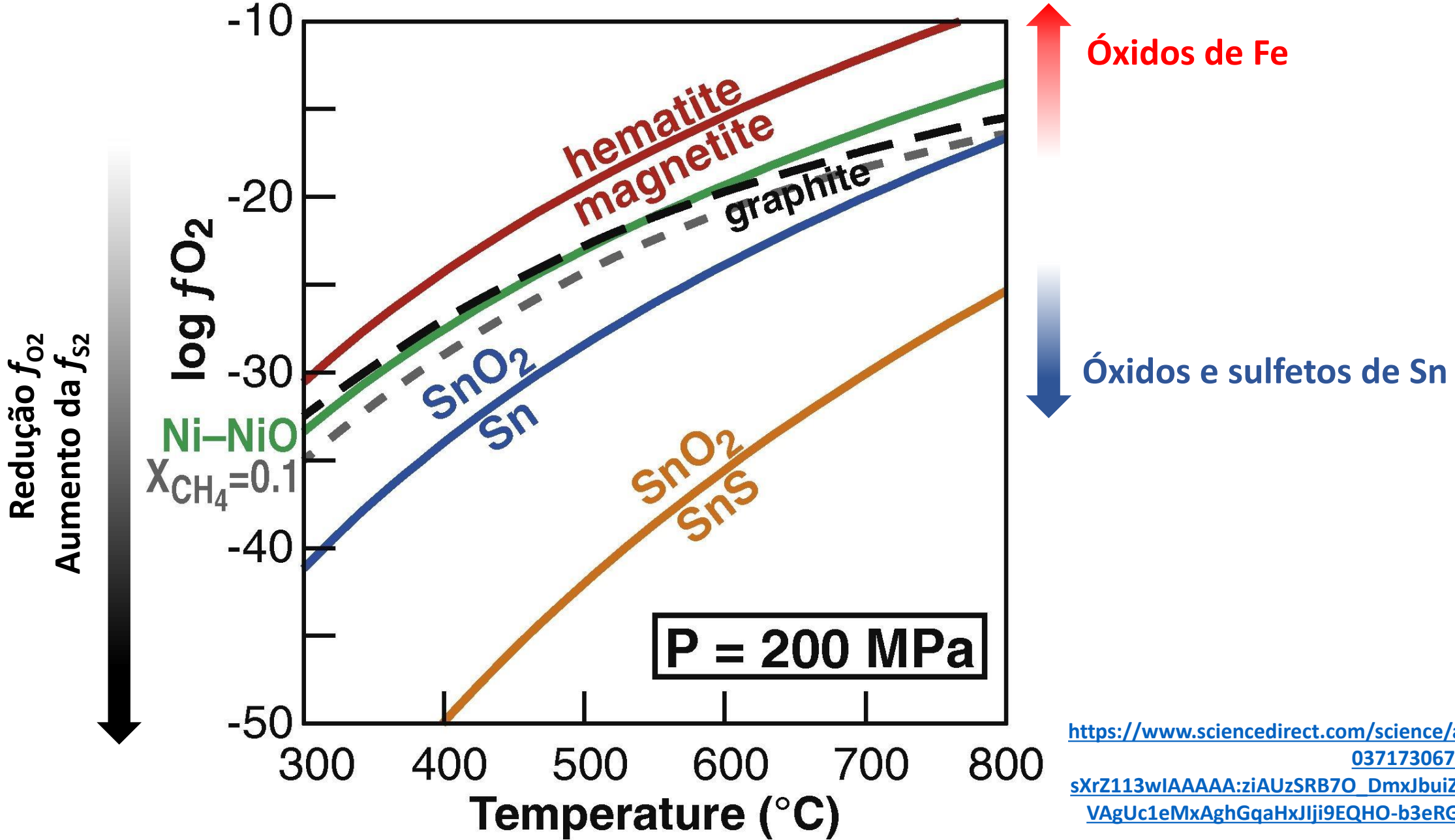


ÓXIDOS DE Sn e W → Greisens Sn-W

"Sheeted veins" in granite, Cligga Head, Cornwall

Detalhe de veios paralelizados no sistema greisen.

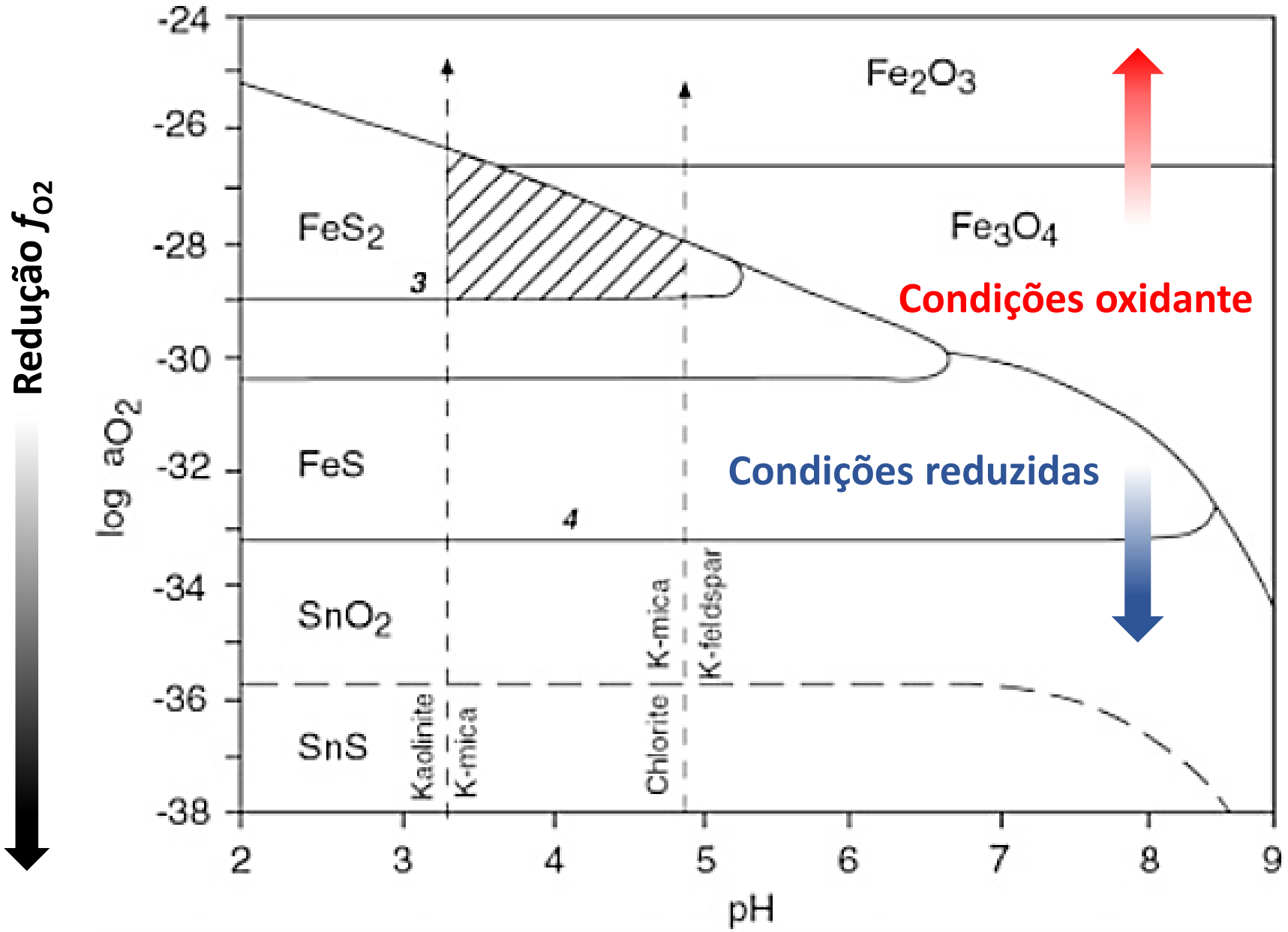
RELAÇÃO ÓXIDOS DE Fe E DE Sn



FONTE:
Schmidt (2018)

https://www.sciencedirect.com/science/article/pii/S0016703717306749?casa_token=7-sXrZ113wIAAAAA:ziAUzSRB7O_DmxJbuiZKydaepXqqiJJGJYiVAgUc1eMxAghGqaHxJIji9EQHO-b3eRGGaRA1u1Y#f0005

DIAGRAMA DE ESTABILIDADE pH *vs.* f_{O2}



Hematita
Fe_2O_3

Magnetita
Fe_3O_4

Pirrotita
FeS

Pirita
FeS_2

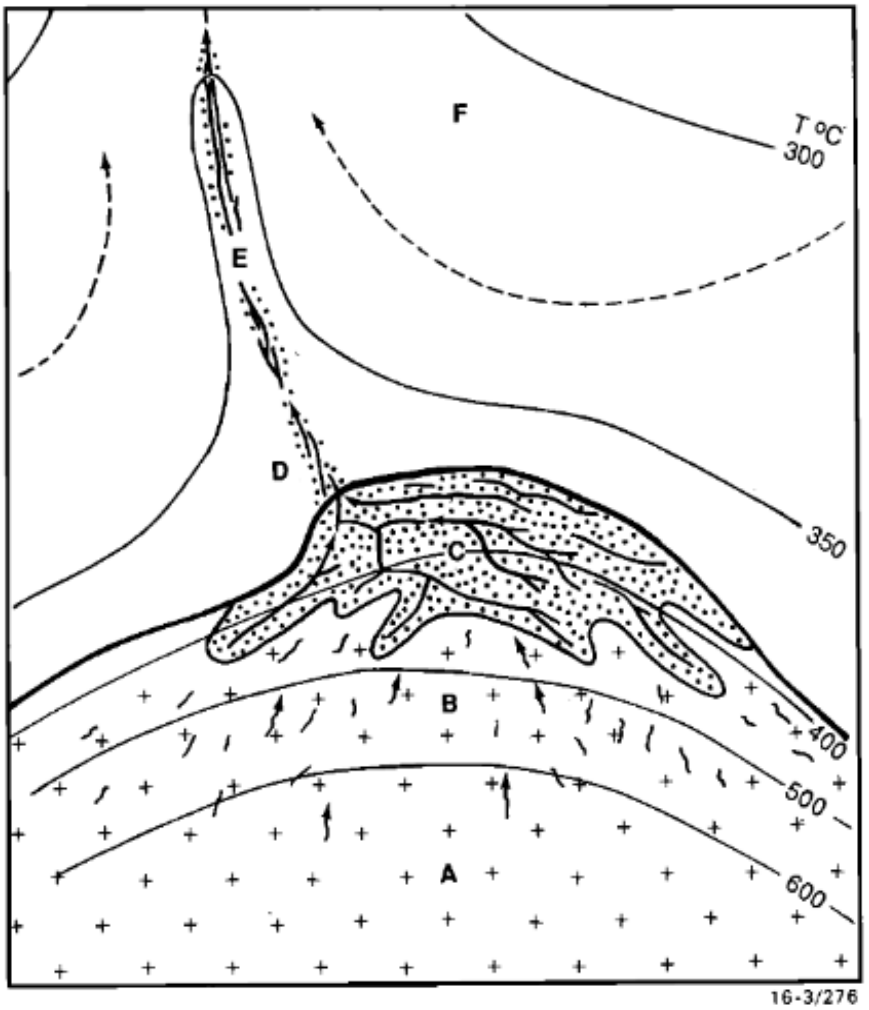
Cassiterita
SnO_2

Herzenbergita
SnS

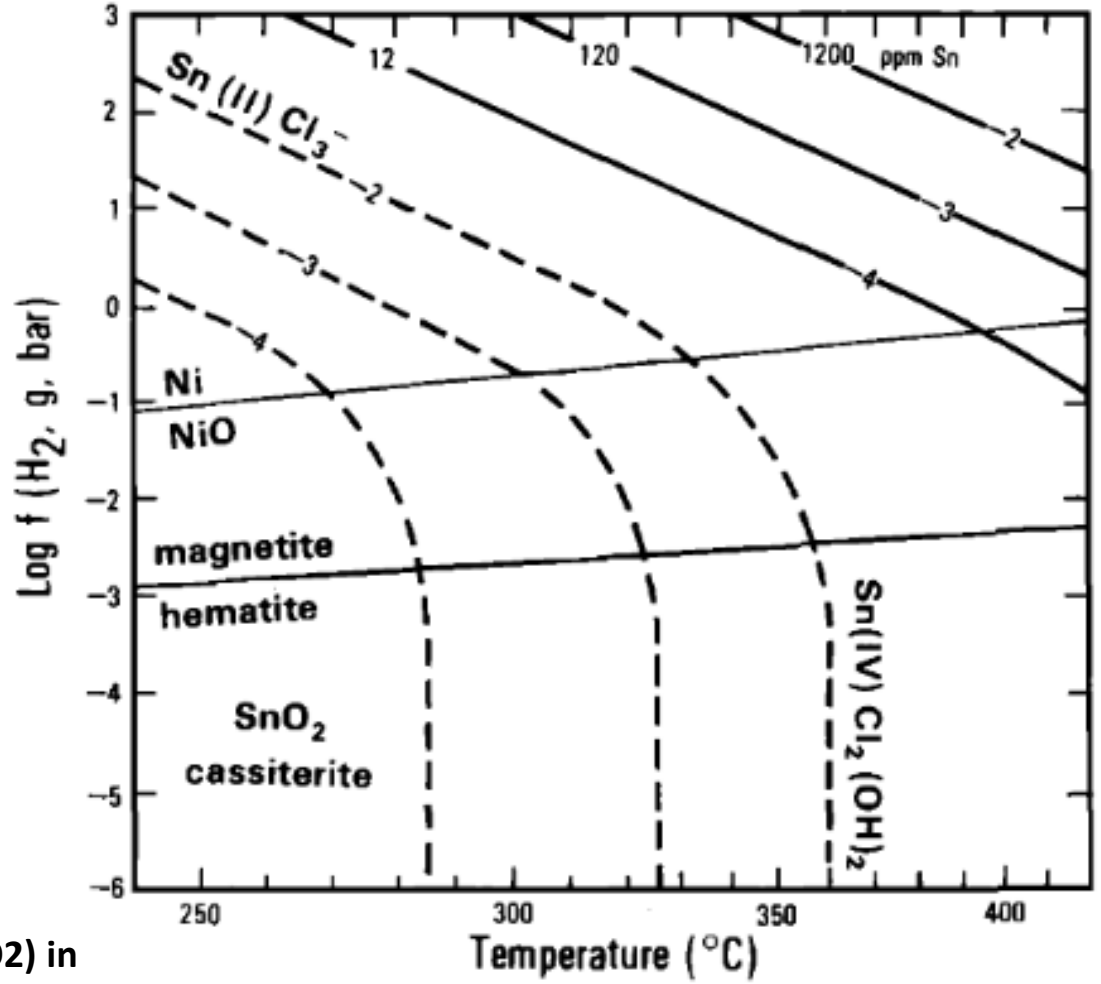
FONTE:
Serranti et al. (2002)

https://rruff.info/uploads/CM40_815.pdf

Solubilidade da Cassiterita em Fluidos Hidrotermais



Cassiterita corresponde a um mineral gerado em **estágios hidrotermais ácidos de sistemas do tipo greisens**, sob **moderadas temperaturas**.

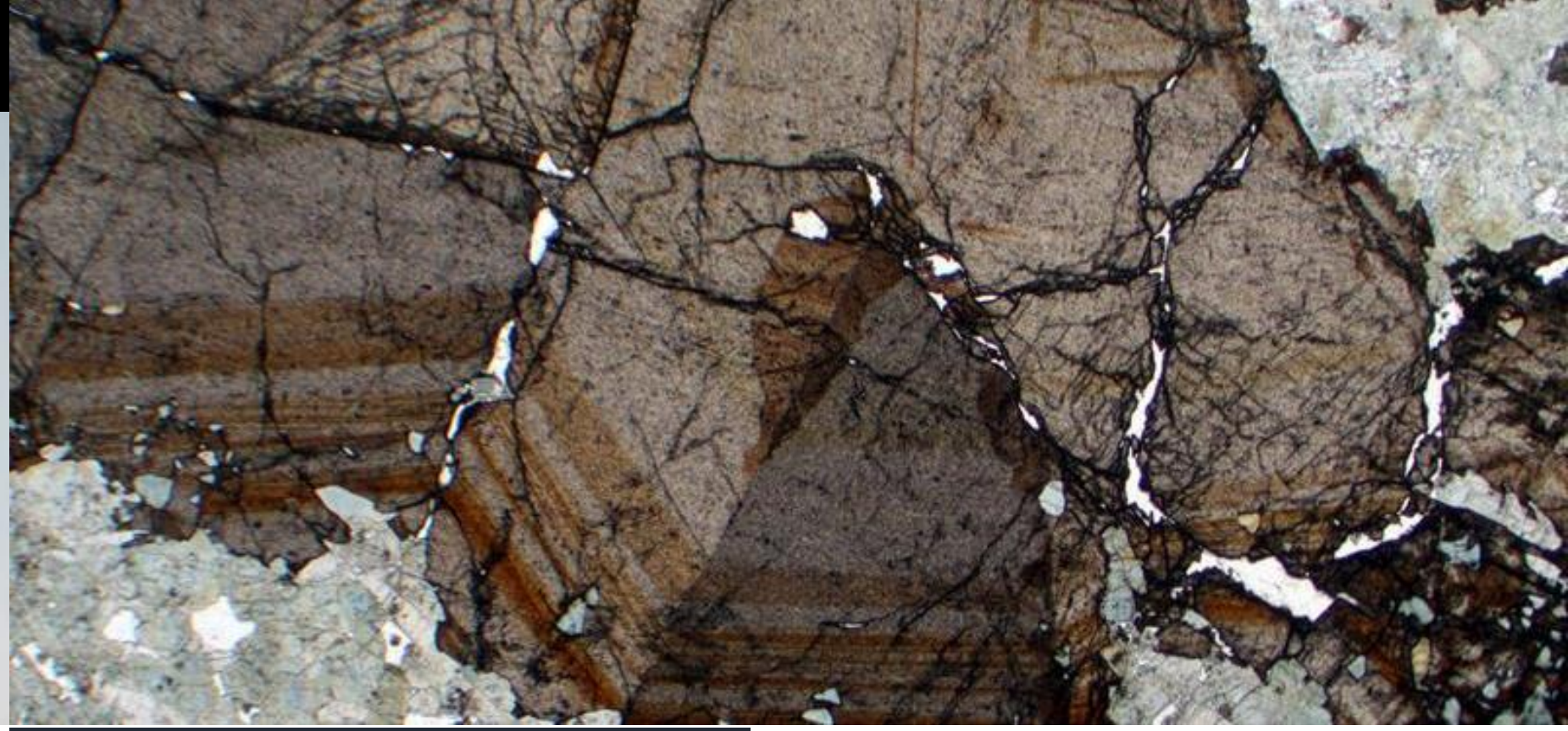


— 2 m Cl_{tot}
+ K-feldspar
+ Albite
+ Muscovite
+ Quartz

— — 2 m Cl_{tot} (K/K + Na) = 0.25
+ Kaolinite
+ Muscovite
+ Quartz

Temperature vs. redox diagram showing contours for the solubility of cassiterite (SnO2) in a 2-m chloride fluid, calcu- lated from data referenced in Table 3 including experiments by Pabalan (1986). Note that high tin solubilities in fluids buffered with regard to acidity by muscovite + feldspars + quartz are re- stricted to high temperatures and/or very reducing conditions (solid lines). High solubilities extend to much lower temperatures in more acid fluids in equilibrium with muscovite and quartz alone (limited by the dashed contours for the buffer assemblage mus- covite + kaolinitc + quartz) (HEINRICH, 1990). ►►

Cassiterita SnO_2



▲ Fonte:
http://www.alexstrekeisen.it/english/meta/cassiterite.php

Heinrich Frank

Cassiterita - Luz Refletida (Polarizadores Descruzados e Cruzados)

https://www.youtube.com/watch?v=hcBDf9hySkY&list=PL5k_2NCH5I4DpfquSi37J4nmHfeiTjDUl

... Em luz transmitida:

Cor
Acastanhada, amarronzada, avermelhada.

Pleocroísmo
Forte pleocroísmo avermelhado, acastanhado.

Relevo
Muito alto.

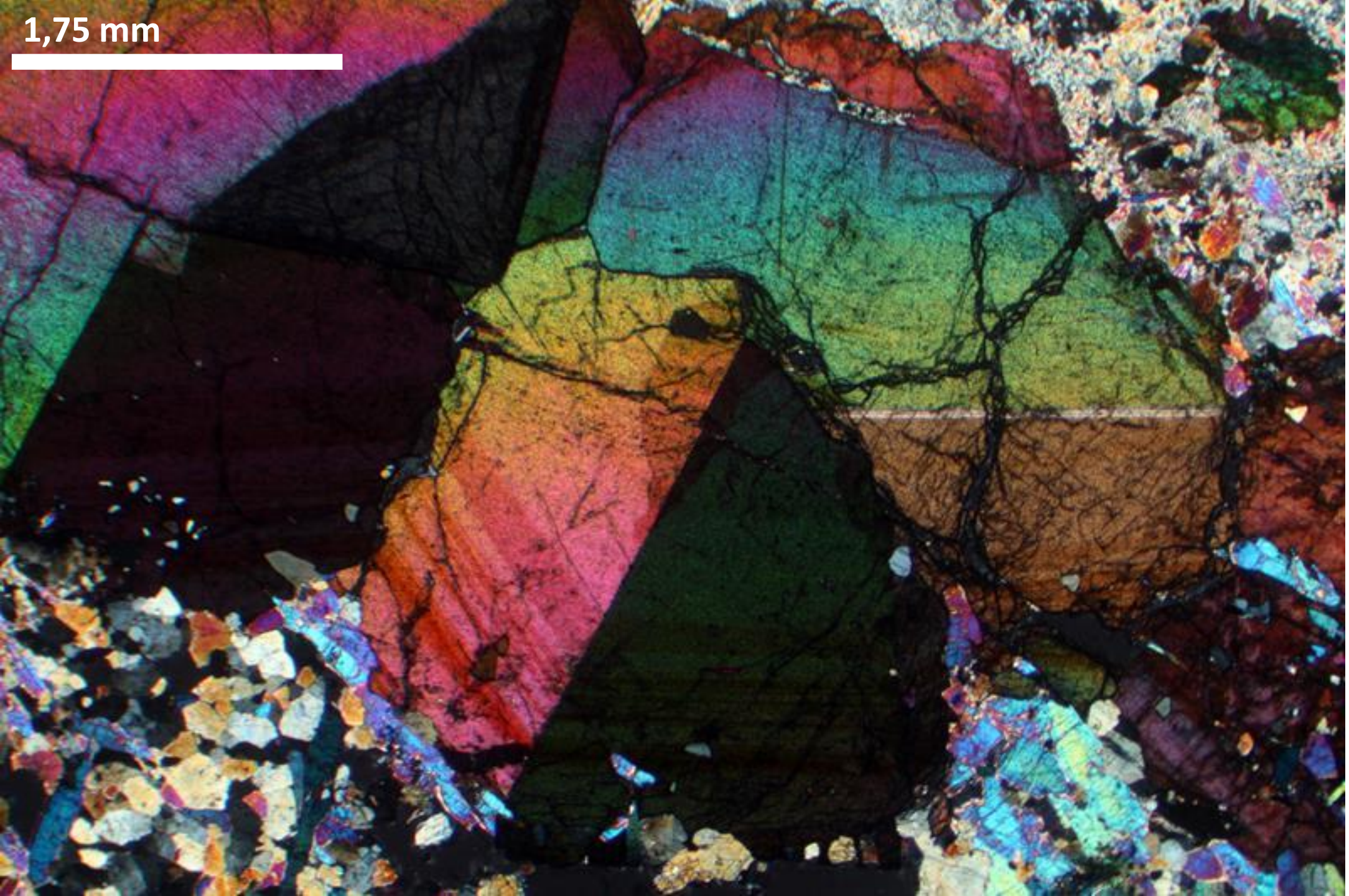
Extinção
Paralela

Cor de Interferência
Cores elevadas.

Outras características
Pode exibir zoneamento.

◄ Zoned cassiterite crystal (brown) and blue tourmaline crystals. St. Just mine, Cornwall. PPL image, 10x (Field of view = 2mm.

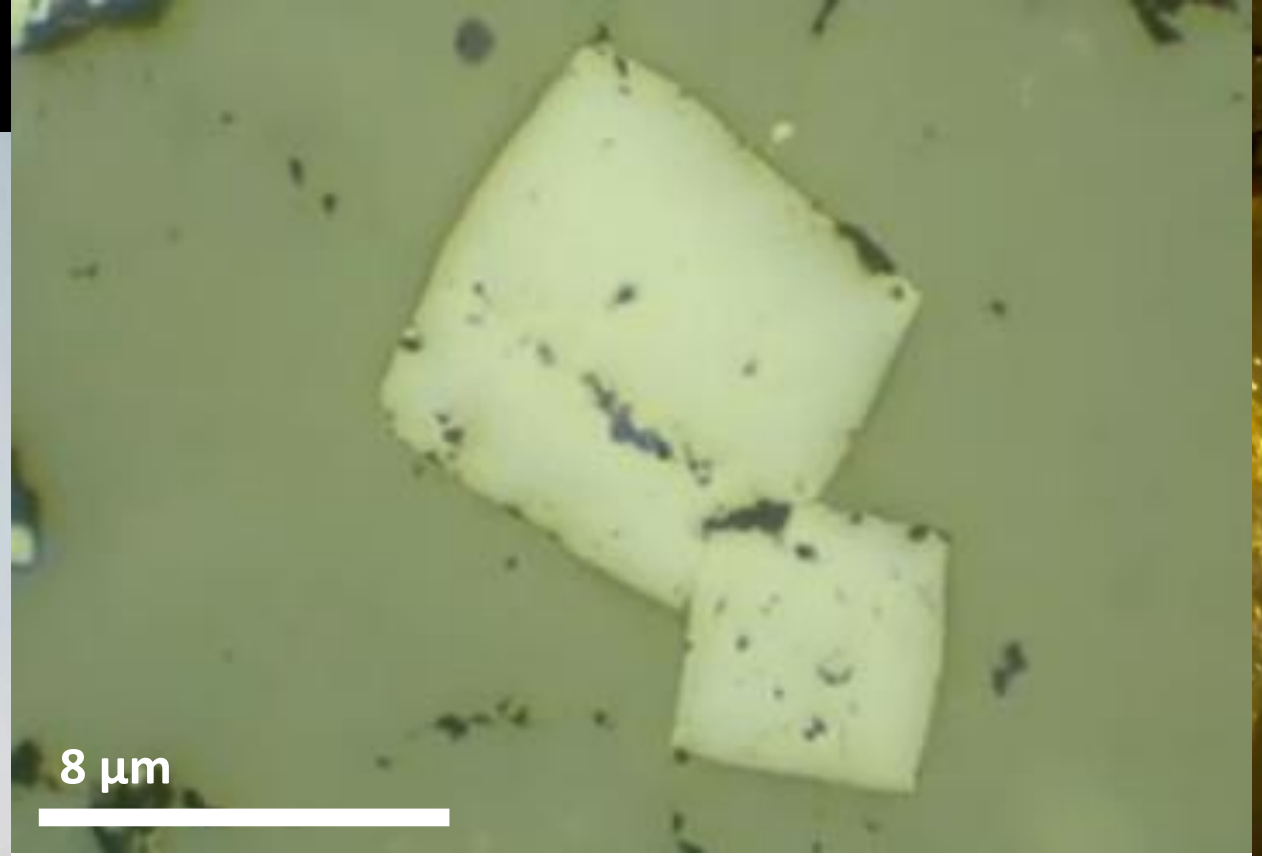
◄ Fonte: http://www.alexstrekeisen.it/english/meta/cassiterite.php

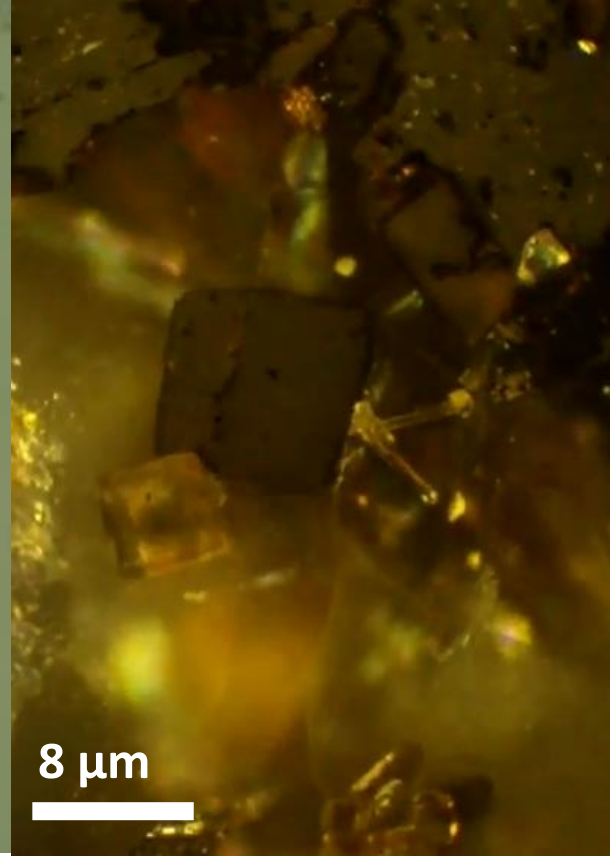


◄ Zoned cassiterite crystals and tourmaline crystals. St. Just mine, Cornwall. XPL image, 2x (Field of view = 7mm.

◄ Fonte: http://www.alexstrekeisen.it/english/meta/cassiterite.php

Cassiterita SnO_2





Heinrich Frank

Cassiterita - Luz Refletida (Polarizadores Descruzados e Cruzados)

https://www.youtube.com/watch?v=hcBDf9hySkY&list=PL5k_2NCH5I4DpfquSi37J4nmHfeiTjDUl

... Em luz refletida:

Cor

Cinza médio (mais claro do que a ganga).

Reflectância

Baixa (~10-12%).

Reflexões internas

Dourado, laranja a amarelo.

Birreflectância

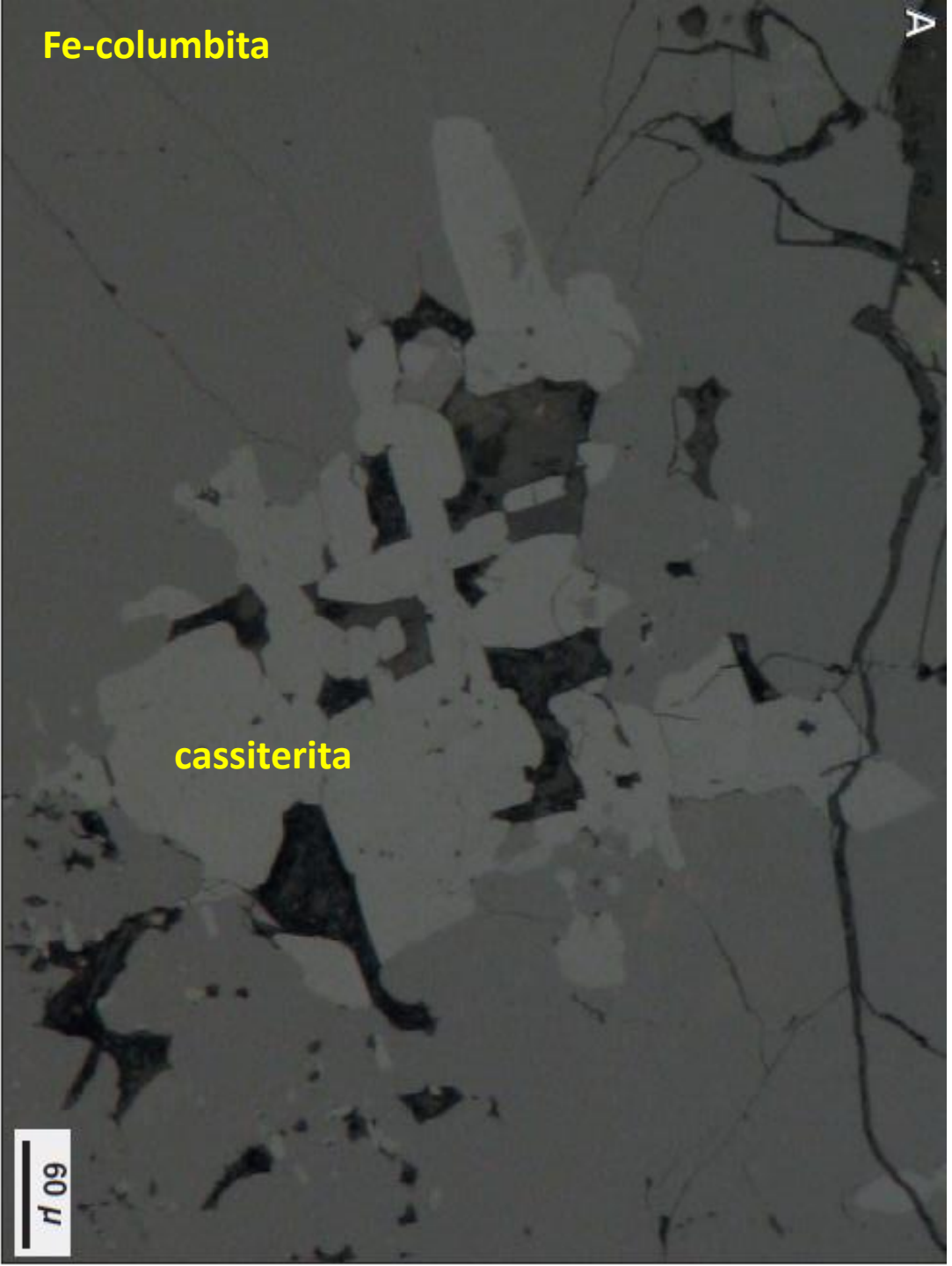
Fraca a forte (limites dos grãos mais fácil de visualizar).

Anisotropia

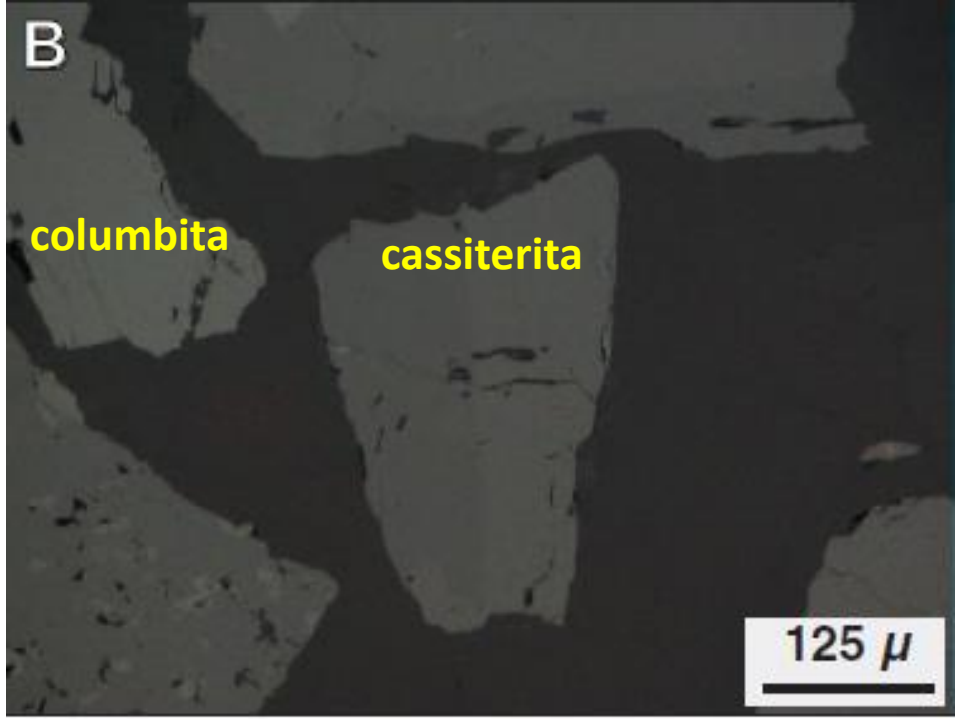
Forte anisotropia em tons de cinza.

Outras Carcterísticas

Buracos por conta do polimento, e maclas.

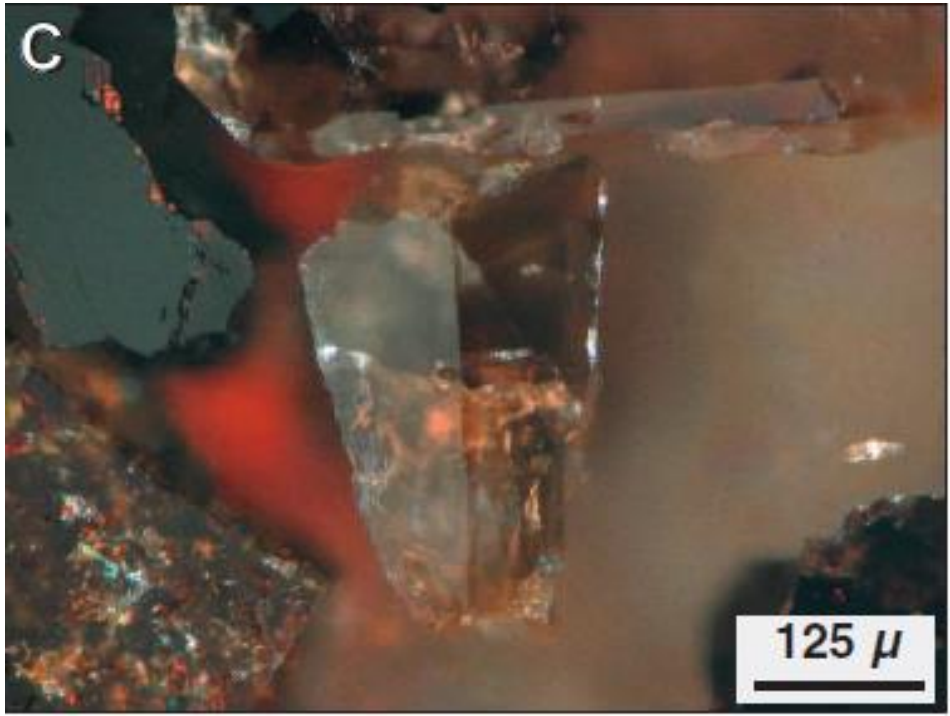


Cassiterite concentrate (grey irregular twinned grains, bireflectance), columbite (upper left, slightly lighter grey than cassiterite); Kazat mine, Merqui, Burma [d]; Nic. // ►

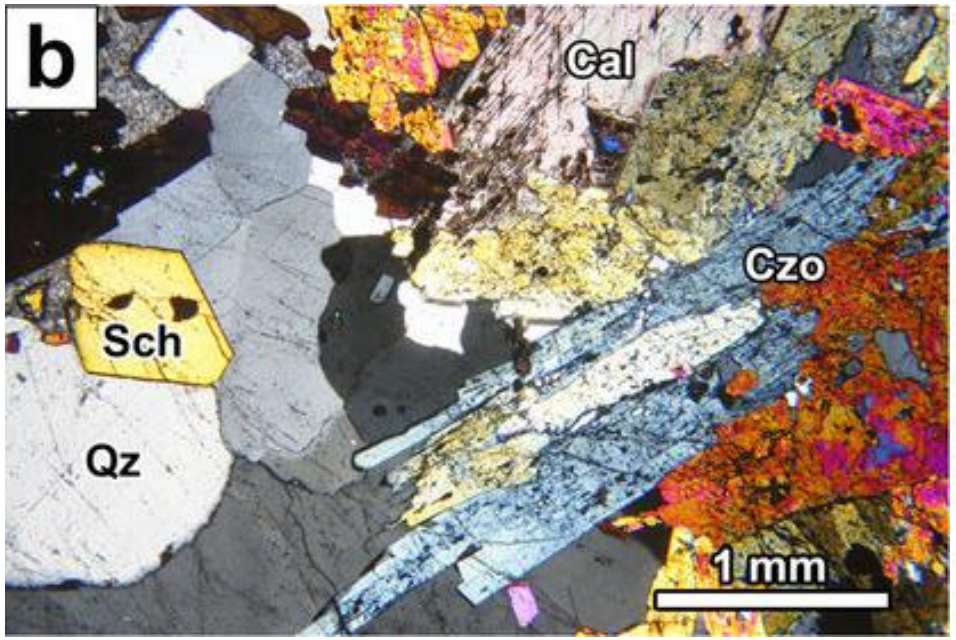


◄ Regular intergrowth of ferrocolumbite (lighter grey) and cassiterite (medium grey); Kazat mine, Merqui, Burma [d]; Nic. //

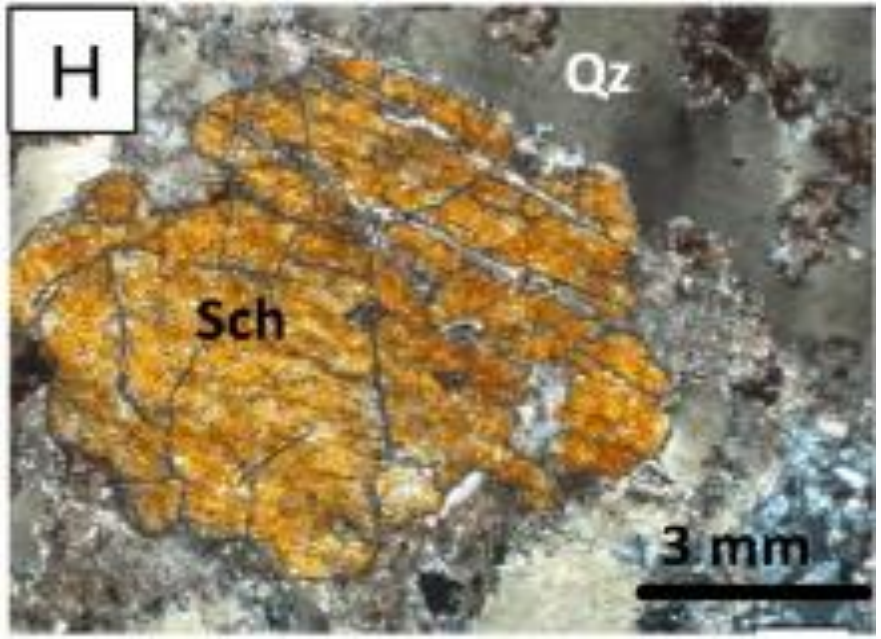
Cassiterite (anisotropy more pronounced), columbite (medium grey, small red to brown internal reflections); Kazat mine, Merqui, Burma [d]; Nic. + (+2°) ►



SCHEELITA $CaWO_4$



▲ FONTE: Raith et al. (2019)



▲ FONTE: Soloviev & Kryazhev (2017)

Heinrich Frank

SCHEELITA - LUZ REFLETIDA (POLARIZADORES DESCRUZADOS E CRUZADOS)

https://www.youtube.com/watch?v=GNlFSsnVb1M

... Em luz refletida:

COR
Cinza branco a cinza médio.

REFLECTÂNCIA
Muito baixa (~10-13%).

REFLEXÕES INTERNAS
Claras esbranquiçadas e incolores. Podem ser rosadas a amarronzadas.

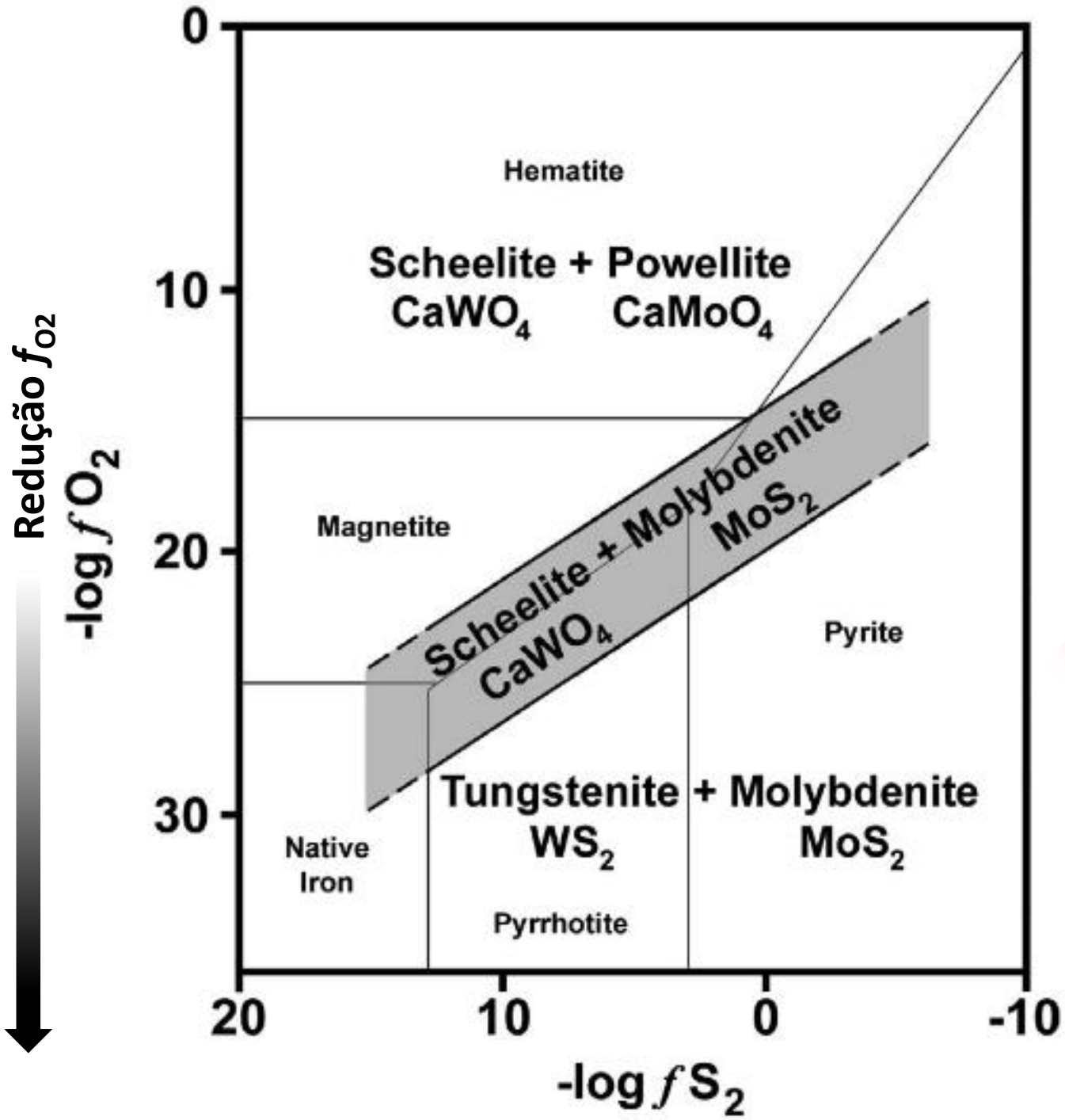
BIRREFLECTÂNCIA
Muito fraca.

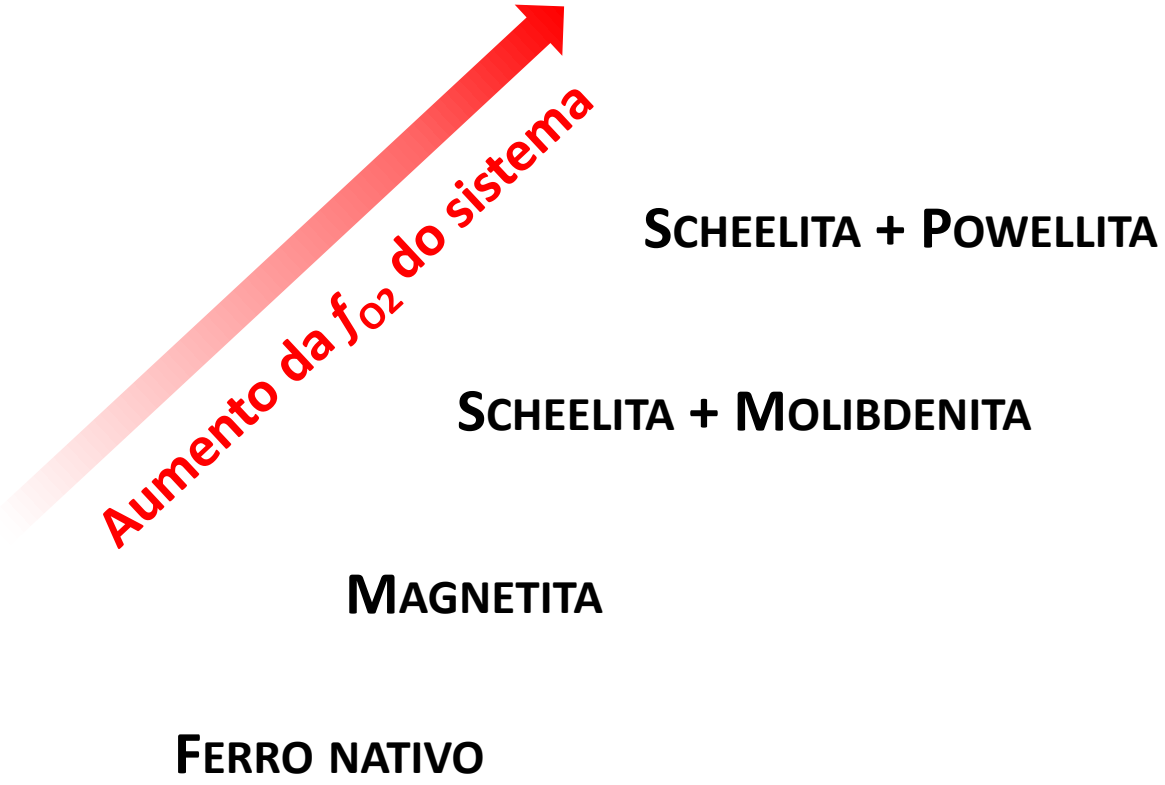
ANISOTROPIA
Ausente.

OUTRAS CARCTERÍSTICAS
Reconhecível sob luz ultravioleta de ondas curtas, sob cores branco azuladas.

Mineral de difícil reconhecimento sob luz transmitida e refletida.

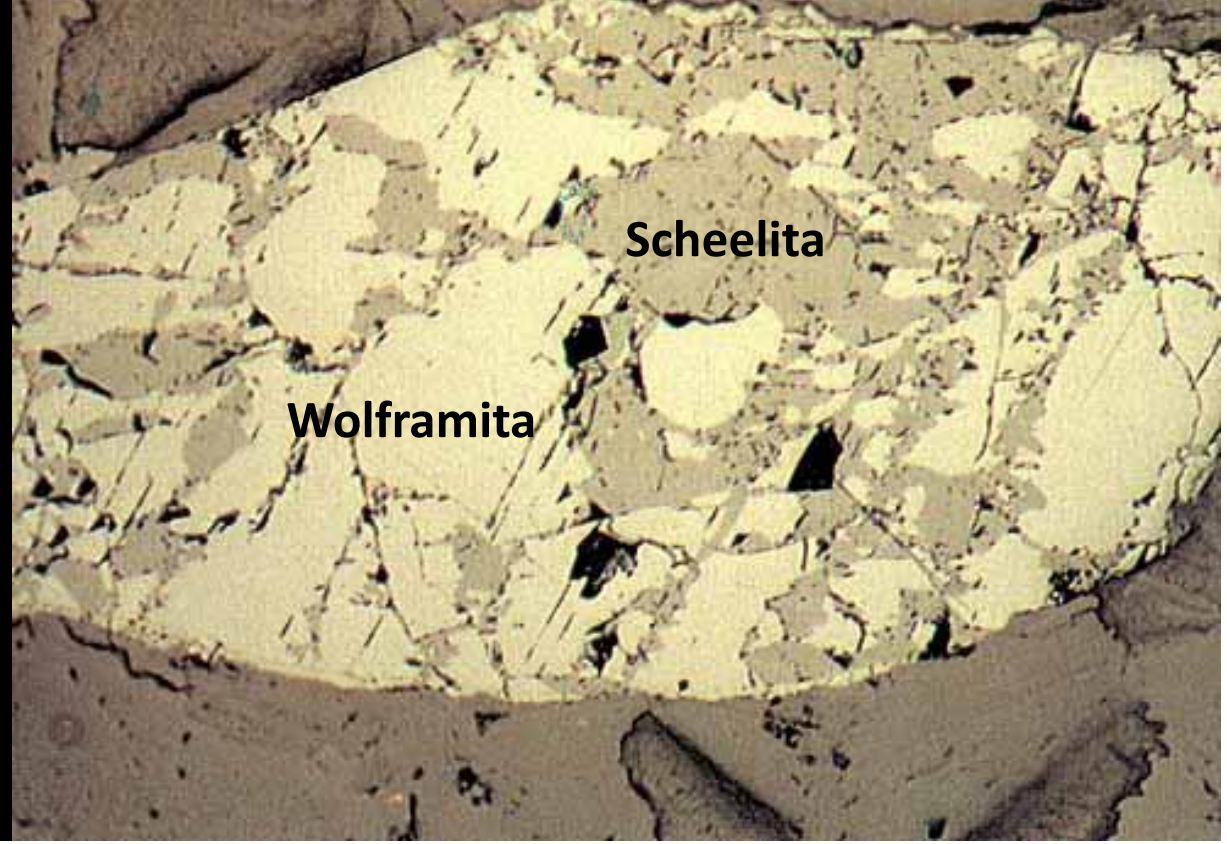
DIAGRAMA DE ESTABILIDADE pH *vs.* f_{O2}





The – logf_{O2} – logf_{S2} diagram indicating thestability field of coexisting scheelite and molybdenite at5778C and 1000 bars fluid pressure (modified from Hsu1977) (From Polin et al., 2016).

WOLFRAMITA $(Fe,Mn)WO_4$



◄ Coarse-grained wolframite (light grey) has been extensively replaced by scheelite (medium grey, centre). Much of the scheelite has a rhombic habit (centre bottom). Feldspar (grey, hard, bottom left) and phyllosilicates (lowest reflectance, poorly polished, top left) are the silicate gangue phases.

Fonte: http://www.atlas-of-ore-minerals.com/plate15e.htm

Heinrich Frank

WOLFRAMITA - LUZ REFLETIDA (POLARIZADORES DESCRUZADOS E CRUZADOS)

https://www.youtube.com/watch?v=oeOIuA-lv9g

https://www.youtube.com/watch?v=q8Lswnf-Ecg

COR

Cinza esbranquiçado, cinza médio (muda em função dos minerais vizinhos).

REFLECTÂNCIA

Muito baixa (~15%).

REFLEXÕES INTERNAS

Raras. Quando presentes marrom-vermelho, vermelho escuro.

PLEOCROÍSMO

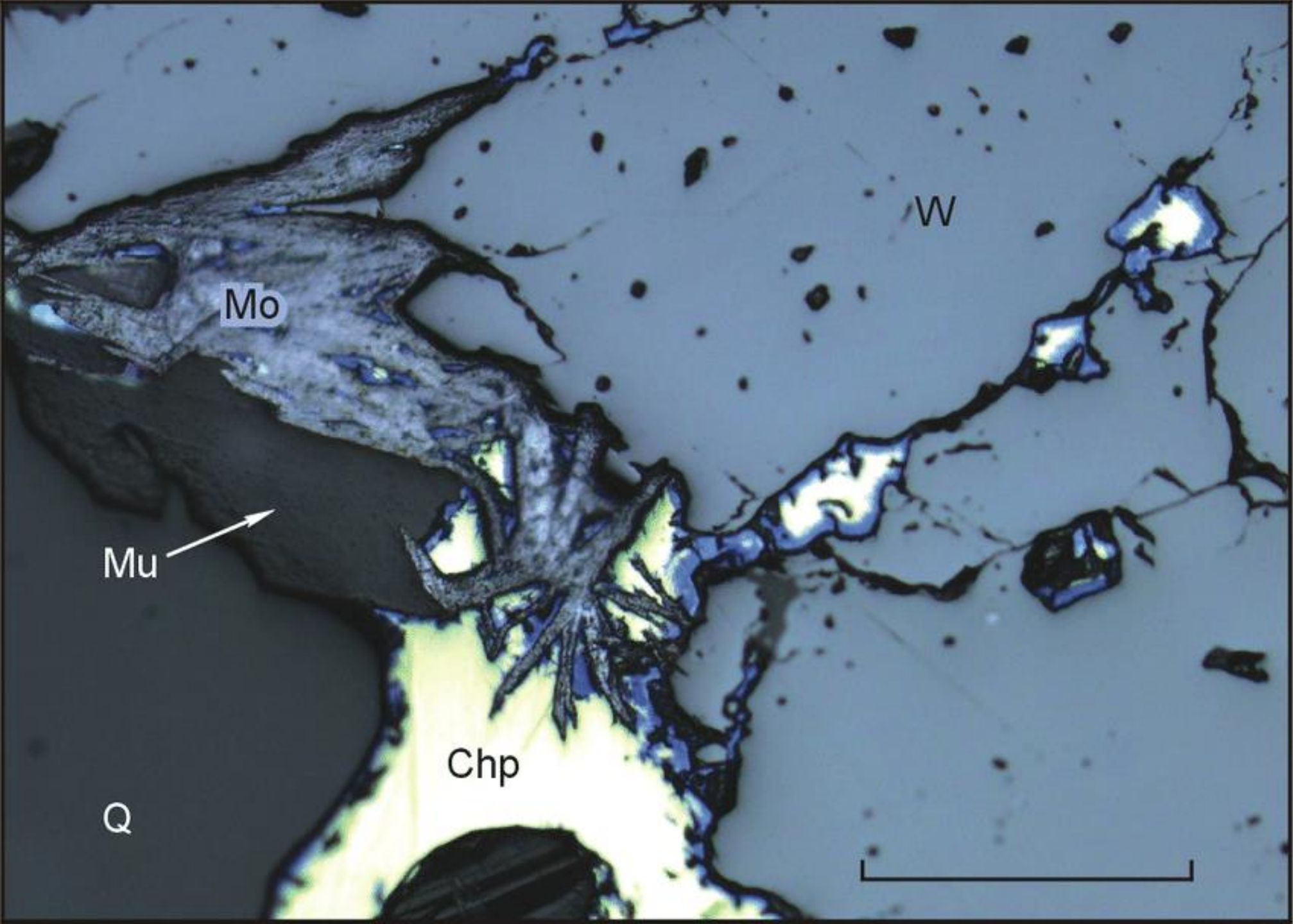
Fraca, discreta.

BIRREFLECTÂNCIA

Fraca, discreta.

ANISOTROPIA

Forte anisotropia cinza esverdeada e marrom escuro (extinção oblíqua).



◄ **Fragment of a coarse wolframite crystal (W) with chalcopyrite (Chp), molybdenite (Mo), and muscovite (Mu) in crash cracks; gray-quartz (Q). Vein 87, thin section; the ruler length is 400 µm.**

FONTE:
Borovikov et al. (2016)