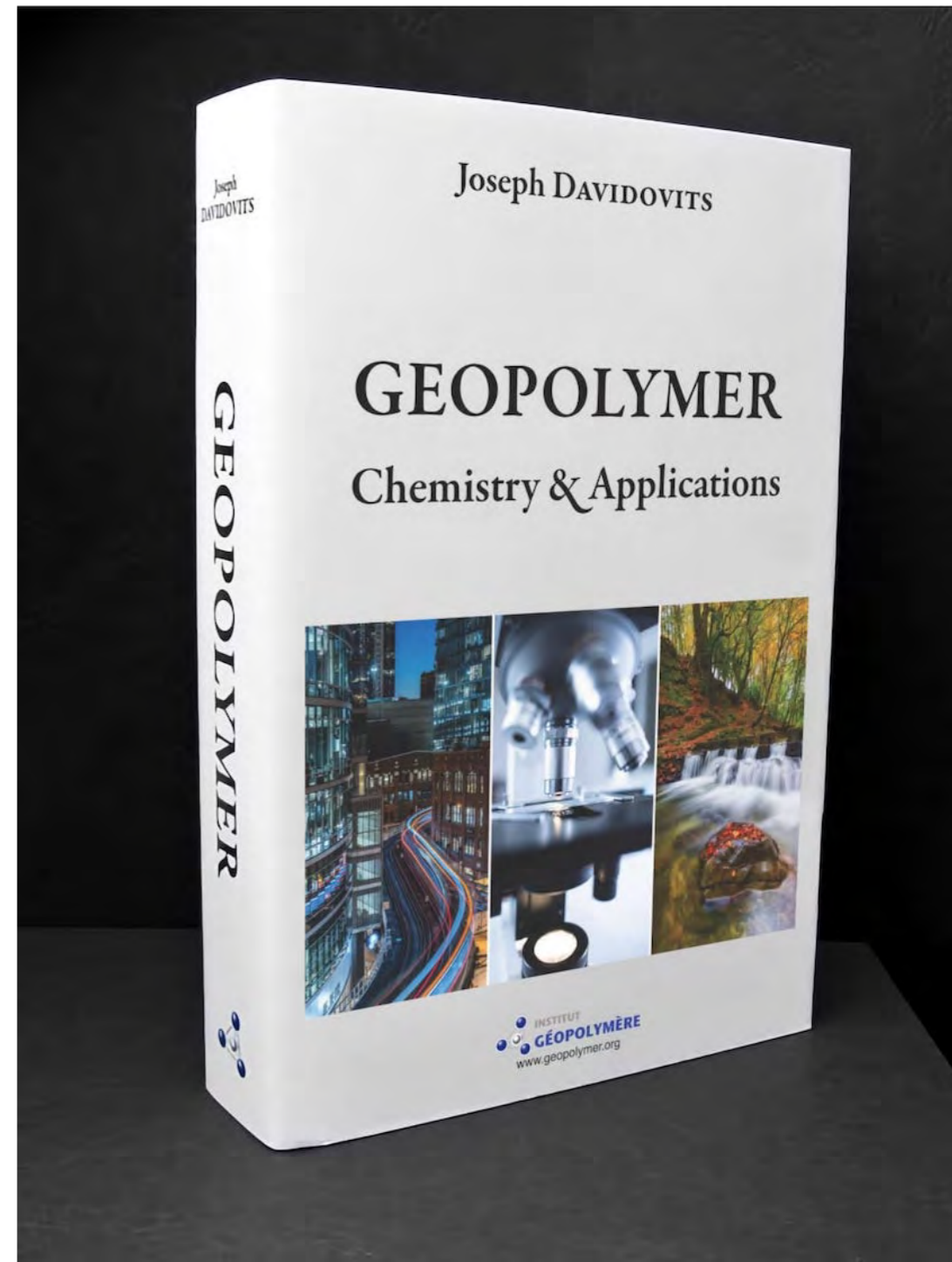




Ferro-sialate geopolymer

Chapter 12



Definition

Ferro-sialate geopolymer designates a binder or cement of the type poly (ferro-silico-aluminate), which has part of the Al atoms substituted by Fe atoms. The Fe atoms are in structural tetrahedral Fe[IV] or pentahedral Fe[V] position in the ferro-sialate sequence [Fe-O-Si-O-Al-O].

Geological raw-materials: red iron-rich rocks or lateritic-clays.

- formed in weathered basic rocks (mafic) :
basalt and gabbro.
- or in weathered acidic rocks :
sandstone, granite or gneiss.

Ferro-sialate [Fe-O-Si-O-Al-O]-based geopolymer binder, results from a geopolymerisation of geological elements rich in iron oxides (Fe^{3+} exclusively) and ferro-kaolinite.

Goethite $\text{FeO}(\text{OH}) + \text{Fe}_2\text{O}_3$ *Hematite* + Fe_3O_4

Magnetite, ranging up to 40 % by weight of the rock.

Geological raw-materials: red iron-rich rocks

- 1) formed in weathered basic rocks (mafic)
basalt and gabbro.





Lateritic rock (not clay) resulting from the weathering of basalt:

12% quartz,

45% kaolinite,

30% hematite, 3% goethite,

10% other elements

(anatase + ilménite+ olivine).

- calcined at 750° C during 3 hours,
- ground to 10-25 microns.

Geological raw-materials: red iron-rich rocks

II) formed in weathered acidic rocks :
sandstone, granite or gneiss,

South American Andes, Altiplano Tiwanaku and *Gate of the Sun* and Pumapunku megaliths.

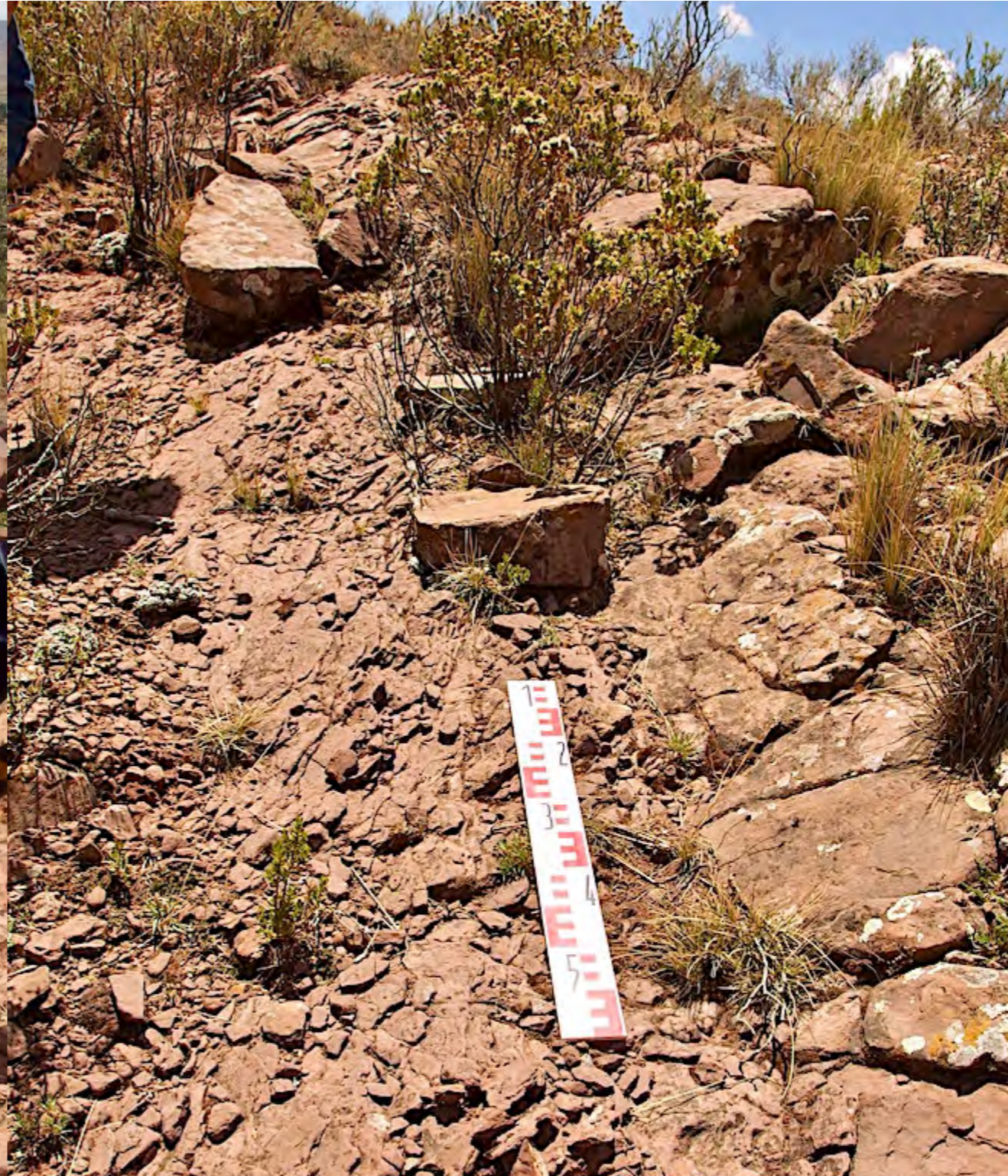


(Na,K,Ca)-(ferro-sialate)-based geopolymer cement

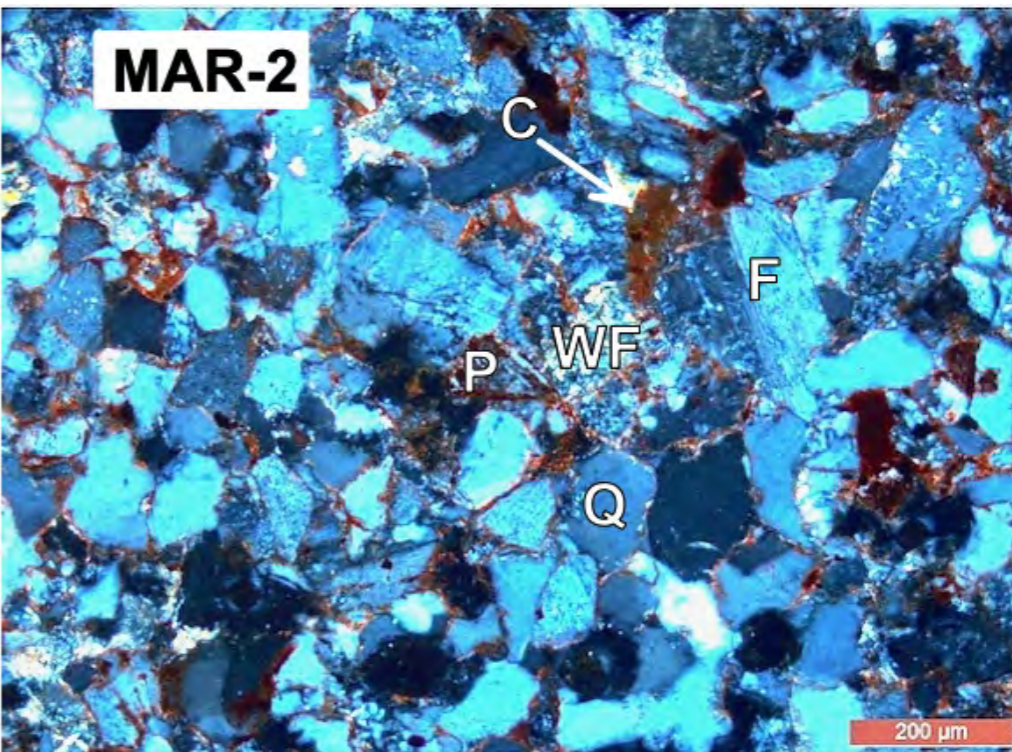
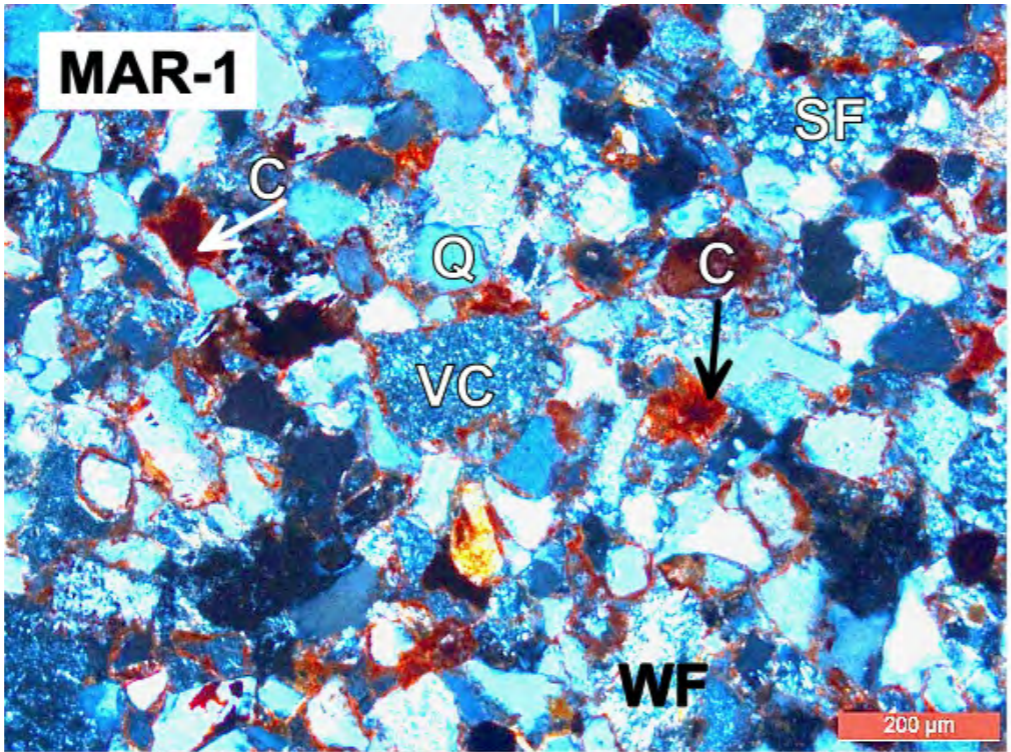
**Pumapunku (Tiwanaku), 1400 years old
Sandstone Geopolymer Concrete**



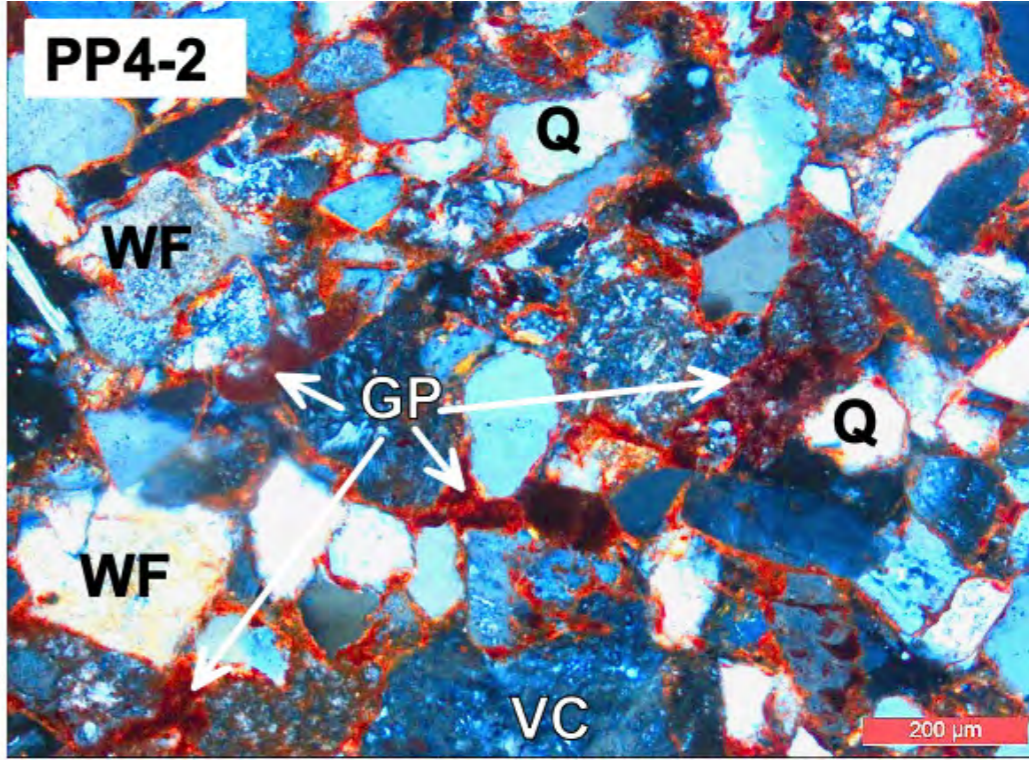
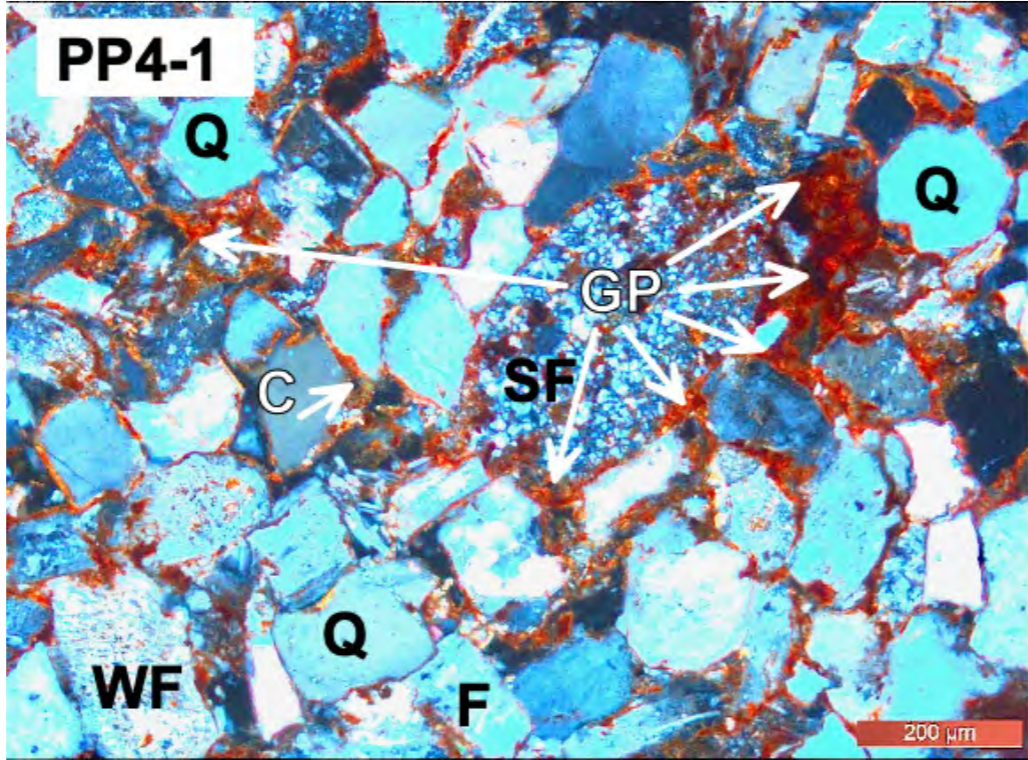
Kallamarka, Bolivia



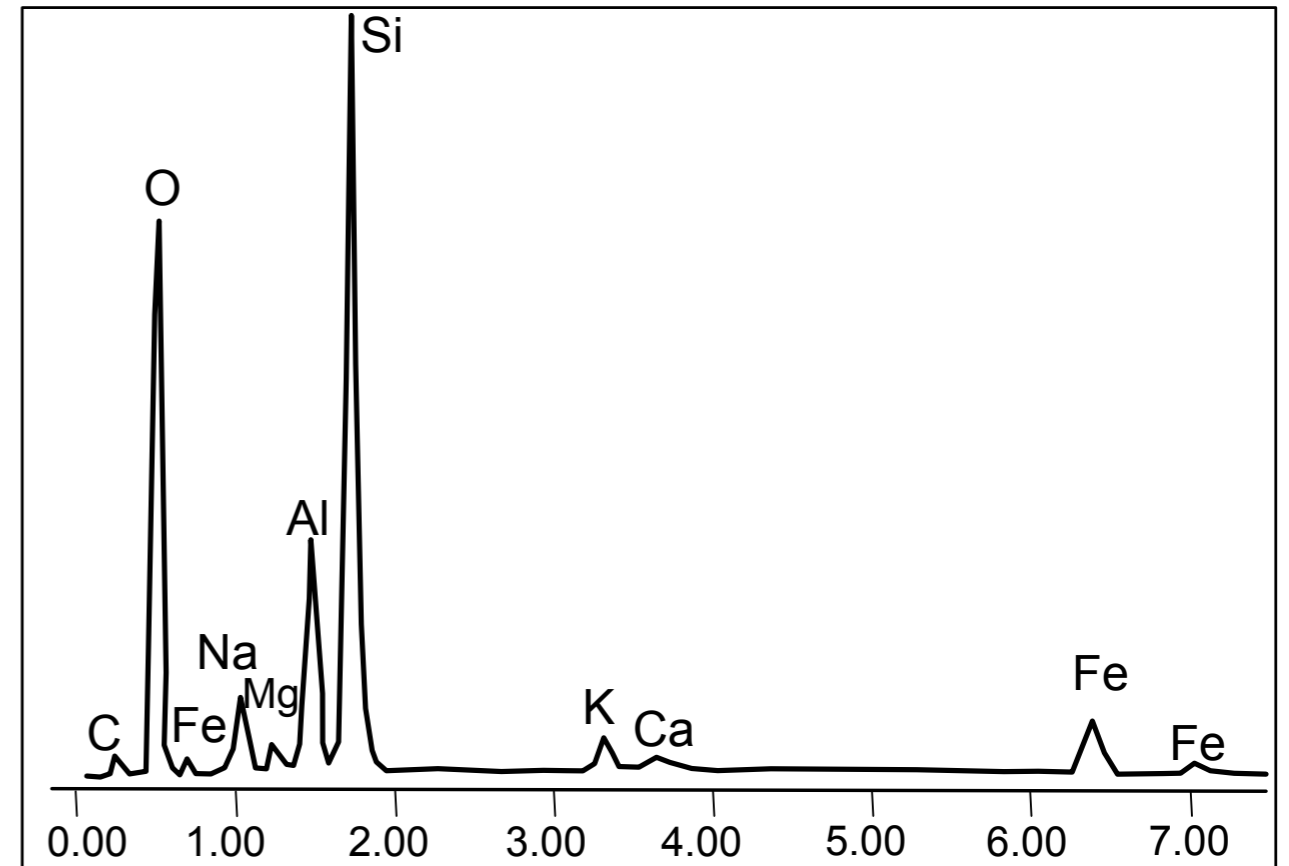
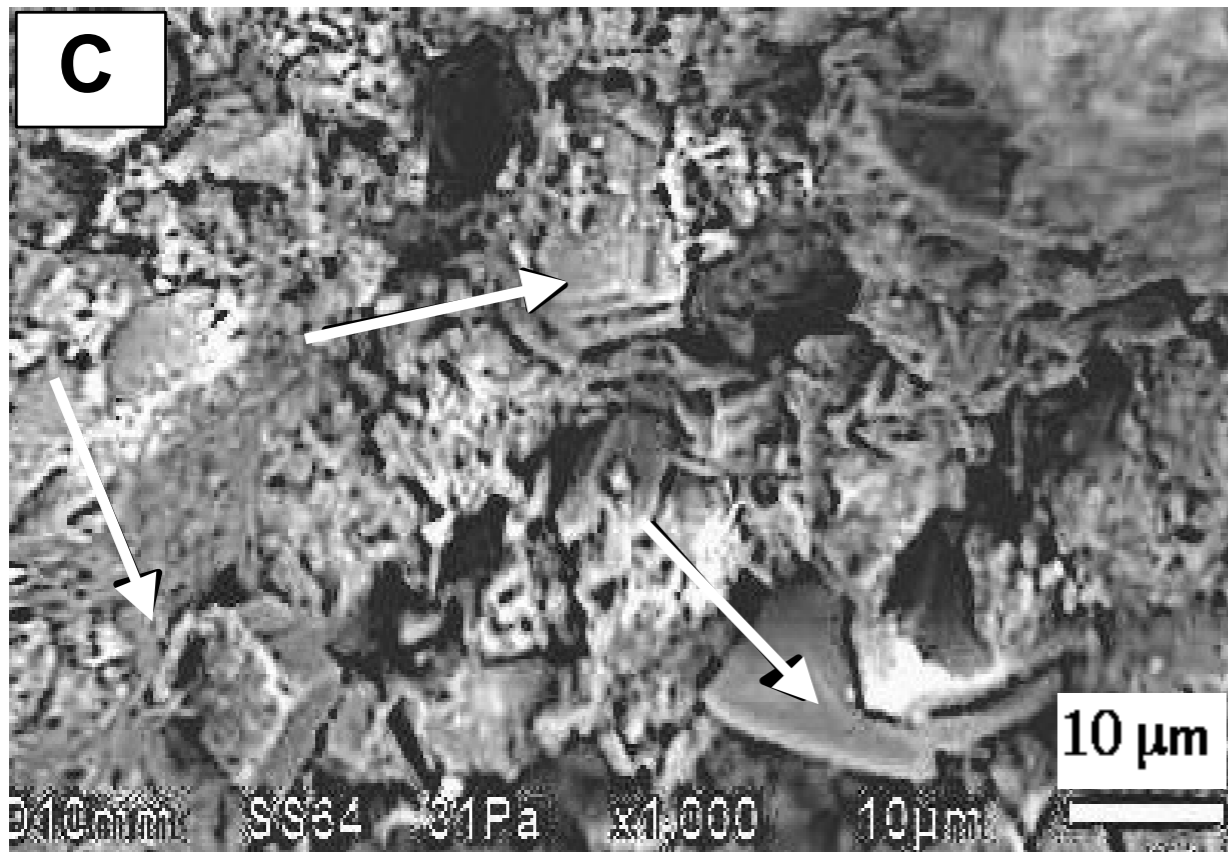
Geological site
Kallamarka



Pumapunku
monument



Pumapunku PP4 matrix



Ferro-sialate matrix between quartz and feldspar grains, with regular geometrical structures (arrows). EDS spectrum of the structures,

Geological raw-materials

Substitution by iron in kaolinite,
P.J. Malden and R.E. Meads, *Nature* 215 (1967) 844-846.

letters to nature

Nature 215, 844 - 846 (19 August 1967); doi:10.1038/215844b0

Substitution by Iron in Kaolinite

P. J. MALDEN & R. E. MEADS

Research Laboratories, English Clays, Loversing, Pochin and Co., Ltd., St Austell, Cornwall.
Department of Physics, University of Exeter.

KAOLINITE often occurs in admixture with other minerals (for example, micas and iron oxides) in which iron is a legitimate constituent. Because of the difficulties of detection and separation, it has always been doubtful whether iron actually substitutes in the kaolinite lattice. We provide here evidence for substitution of iron(III) in the octahedral

References

1. Weaver, C., W.
2. Kündig, W., B.

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KAOLINITE often occurs in admixture with other minerals (for example, micas and iron oxides) in which iron is a legitimate constituent. Because of the difficulties of detection and separation, it has always been doubtful whether iron actually substitutes in the kaolinite lattice. We provide here evidence for substitution of iron(III) in the octahedral (Al) sites.

Geological raw-materials

This substitution occurs only when Fe is the *trivalent Fe³⁺*

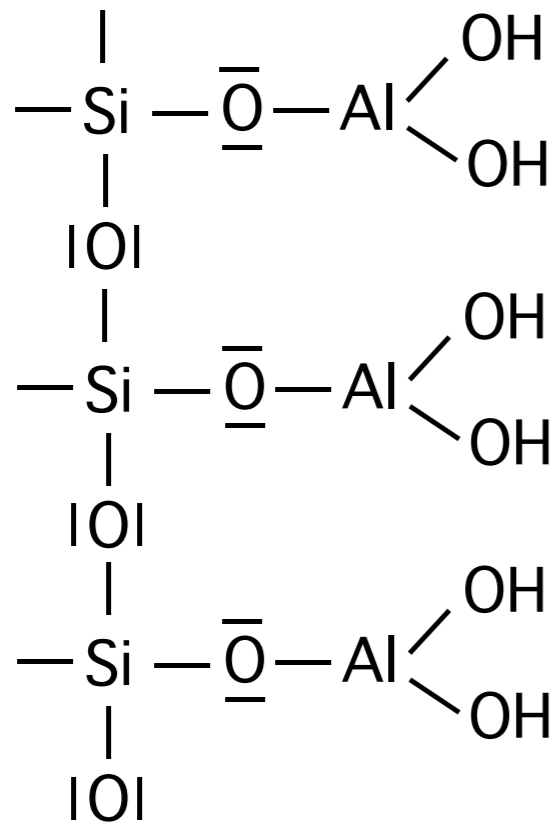
This substitution can reach 25% of the Al atoms, transforming the sequence

$\equiv\text{Si-O-Al(OH)}_2$ of kaolinite into $\equiv\text{Si-O-Fe(OH)}_2$.

It is however impossible to separate the substituted kaolinite from that not-substituted.

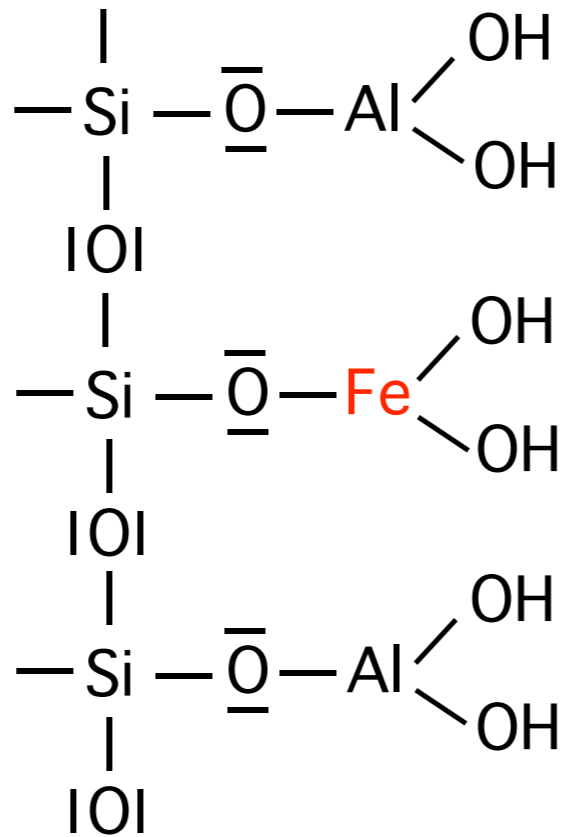
This explains why, we designate the mixture of substituted kaolinite + not-substituted kaolinite by the generic term

“ferro-kaolinite”.



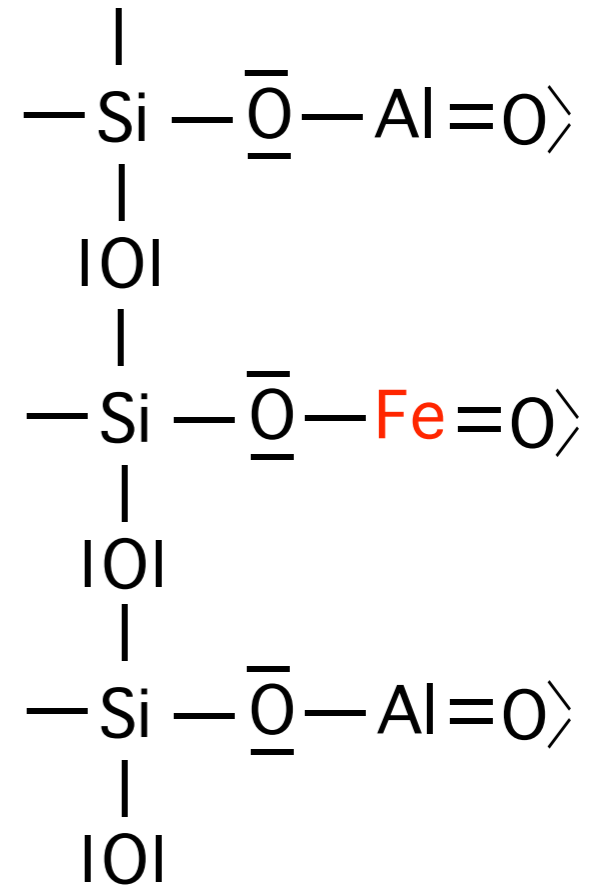
kaolinite

~~NMR spectroscopy~~



ferro-kaolinite
25% Fe/Al
substitution

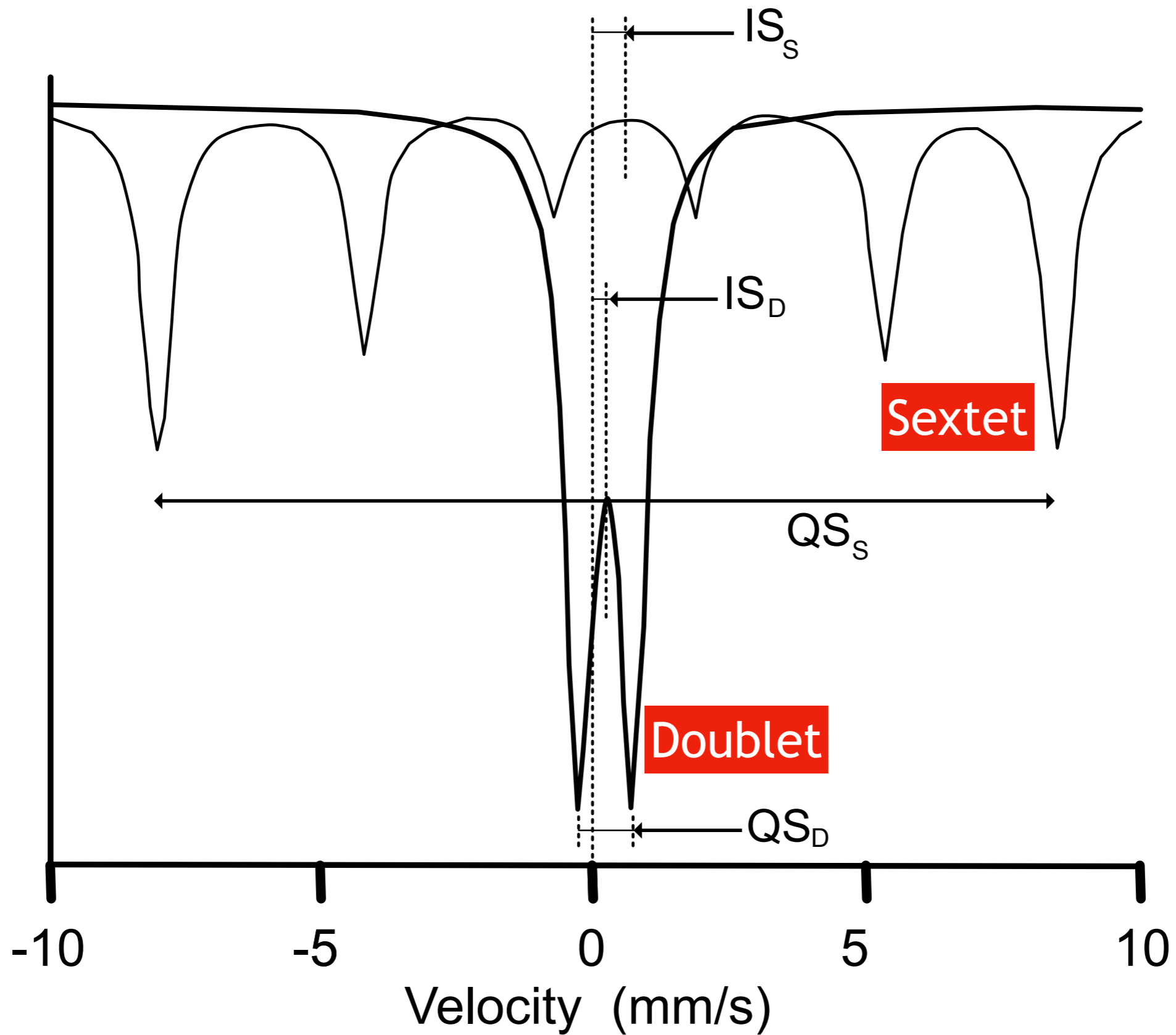
750°C
→



ferro-metakaolinite ?
Fe-MK-750

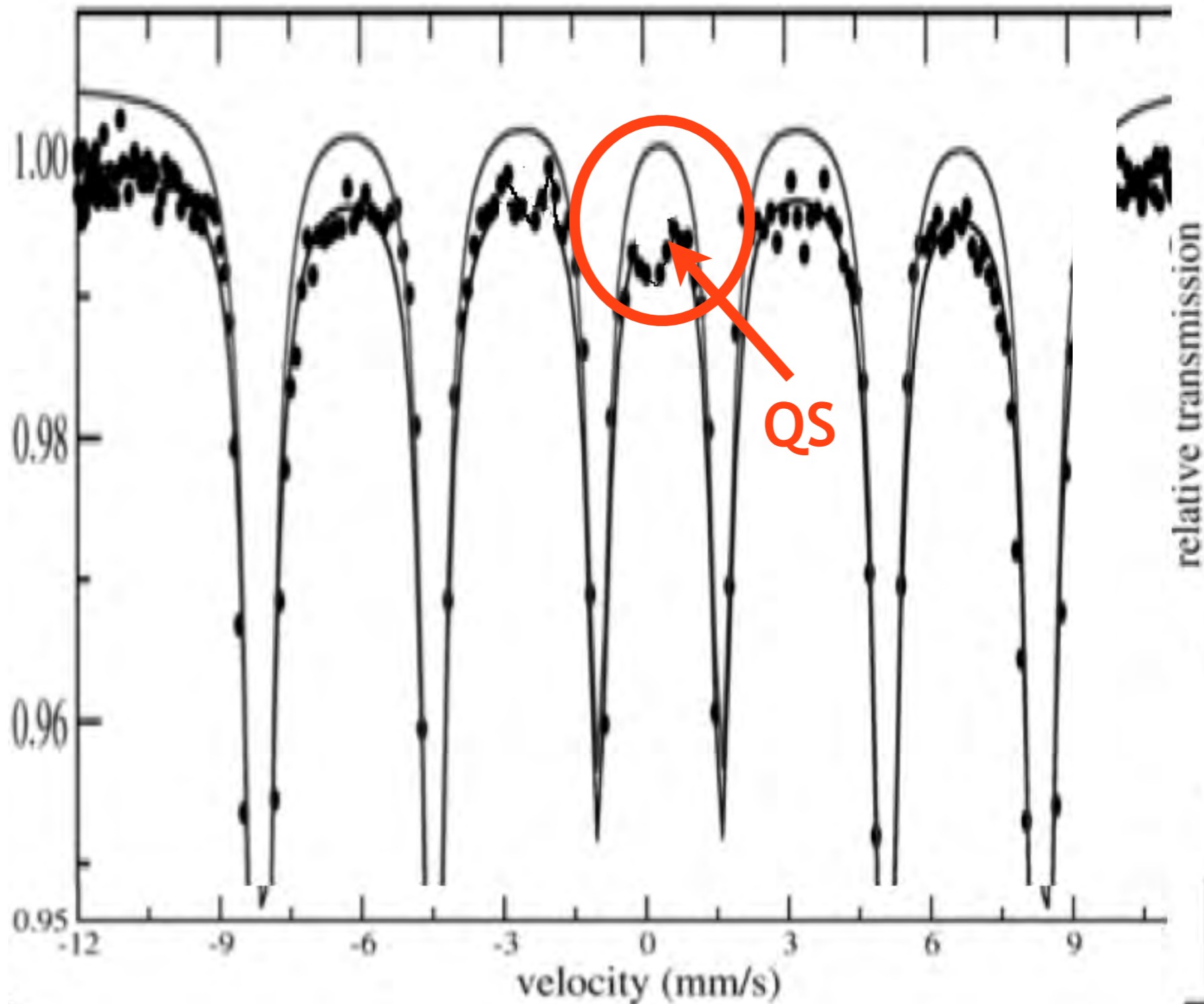
Mössbauer spectroscopy

^{57}Fe Mössbauer Spectroscopy



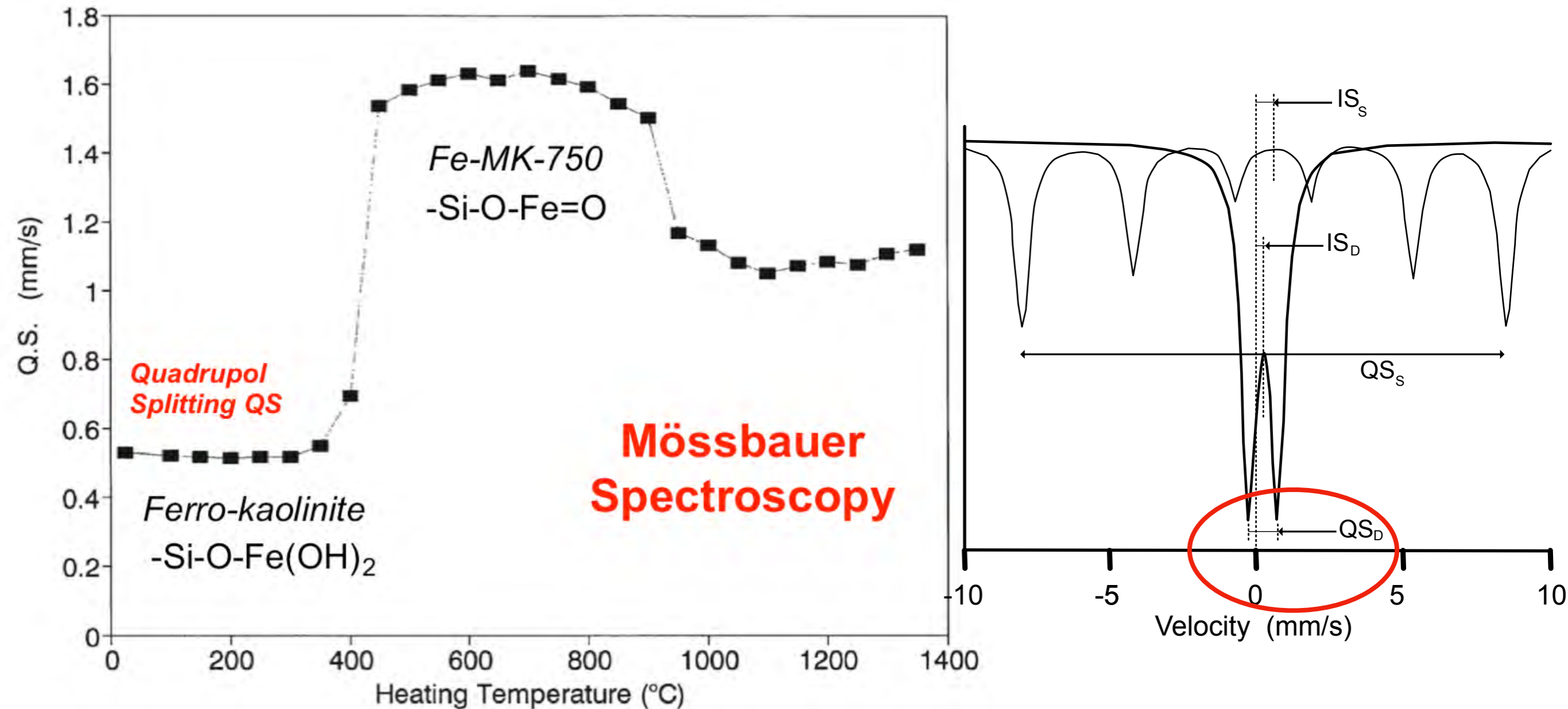
Mössbauer Spectroscopy (ferro-sialate)-geopolymer

adapted from K. C. Gomes et al., *Materials Science Forum* (2010)



Transformation of ferro-kaolinite into Fe-MK-750

adapted from E. Murad and U. Wagner, *Hyperfine Interactions* 117 (1998)



How to calculate substitution Fe / Al

**Pumapunku
ferro-sialate
geopolymer
matrix**

SEM/EDS	atom %	Oxide	Oxide %
Na	7.63	Na ₂ O	8.17
Mg	1.87	MgO	1.24
Al	15.43	Al ₂ O ₃	23.16
Si	59.12	SiO ₂	50.33
K	3.7	K ₂ O	3.54
Ca	0.6	CaO	0.33
Fe	11.65	Fe ₂ O ₃	13.22
	100		100

substituted Fe at. % : 3.86 (max. 25% of Al) in ferro-sialate geopolymer with Si/(Al,Fe) = 3 and rest 7.79 Fe₂O₃ hematite as filler.

Geopolymer Ferrosialate

Ratio K/Al=1 and K/Fe=0.2

Si/Al=2 for a rigid 3D macromolecular structure

100 g of liquid silicate \times a % K_2O in liquid \times 101.96 g/mol Al_2O_3

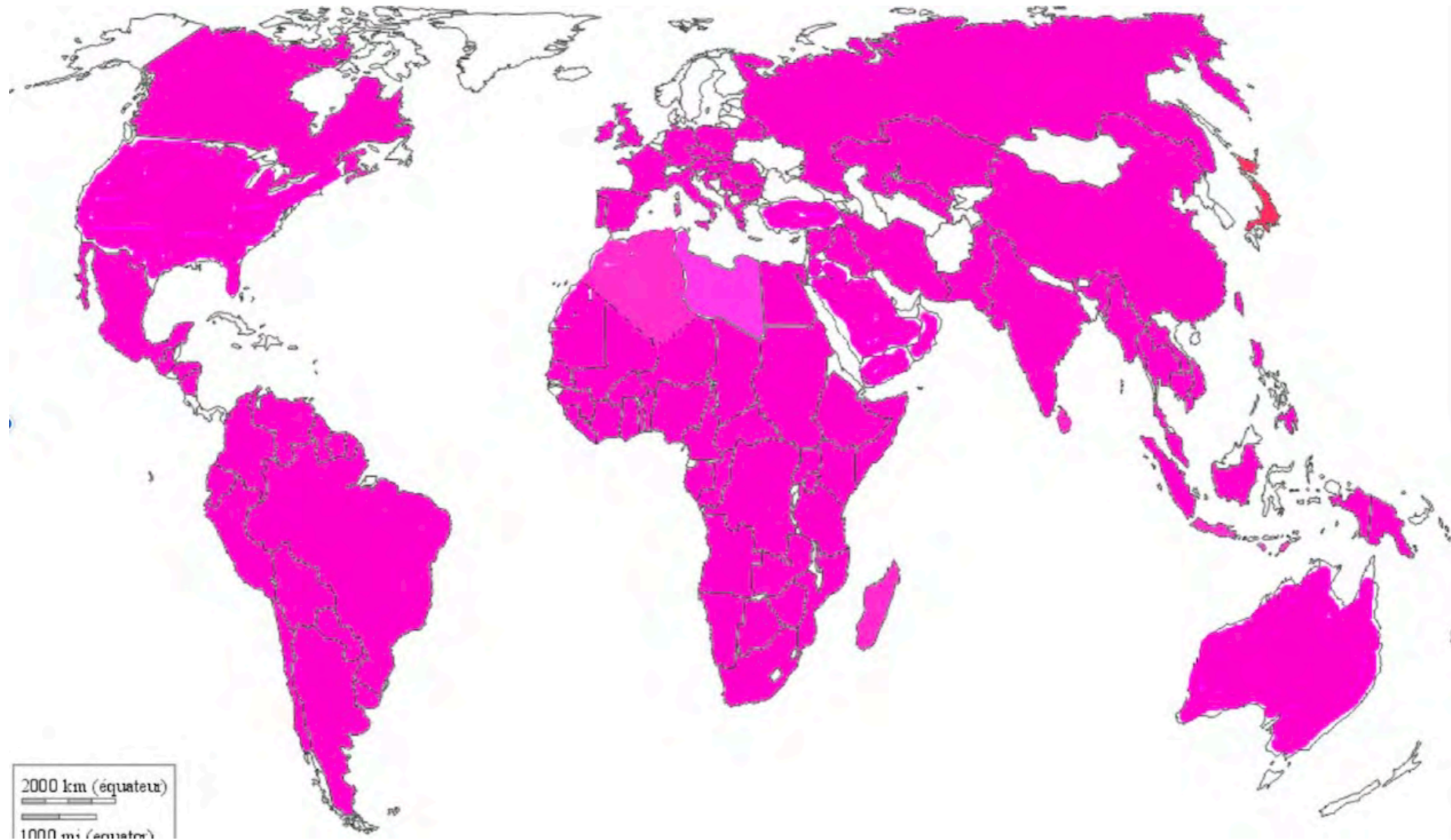
$$\frac{100 \text{ g of liquid silicate} \times a \% K_2O \text{ in liquid} \times 101.96 \text{ g/mol } Al_2O_3}{94.196 \text{ g/mol } K_2O \times \left(\left(\frac{101.96 \text{ g/mol } Al_2O_3 \times b \% Fe_2O_3}{156.58 \text{ g/mol } Fe_2O_3} \right) + \frac{c \% Al_2O_3}{5} \right)}$$

adding the equivalent Al_2O_3

Fe_2O_3 = Hematite not Goethite

Result: for 100 g of silicate, add xx g of ferro-metakaolinite

World-wide availability of raw material for ferro-sialate geopolymer cement



Ferro-sialate geopolymer

Joseph Davidovits