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# Stabilization of lead in incineration fly ash by ageing and carbonatation in contact with moisture and air

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TEKEDO

Presented by
Rolf Sjöblom

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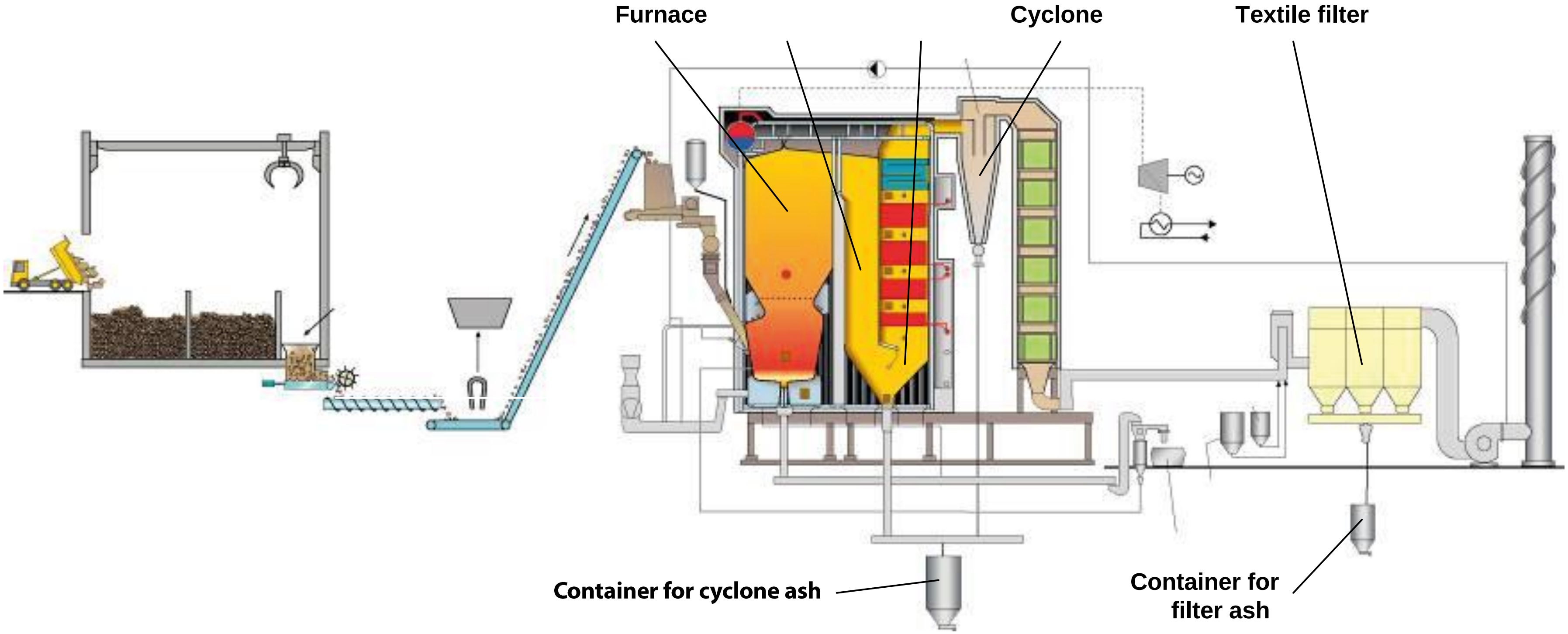
# Underlying permit question

- ***Jönköping Energi AB*** in Sweden operates an incinerator that burns domestic and industrial waste
- It generates fly ash that contains the ”actual” fly ash + lime added to absorb HCl and $SO_2$
- They want to deposit this residue at their local landfill operated by ***Miljöhantering i Jönköping AB***
- The landfill has a permit for disposal of non-hazardous waste

# Fly ash and other ashes



Fractional condensation of volatile elements and compounds.

Partial melting of the ash and consequent formation of reactive glass phase

# How can the ash qualify for disposal at a landfill for non-hazardous waste?

| | |
|---|---|
| As non-hazardous waste | In which case the fly ash can be deposited at a landfill for non-hazardous waste without any so-called “basic characterization” |
| As hazardous waste | In which case the fly ash will have to qualify under the leach and other criteria in the legislation on acceptance for landfilling |

| | |
|---|---|
| Classification as hazardous of non-hazardous waste | The content of chemical substances and their respective hazardous properties |
| Acceptance for landfilling, detaled rules | Mainly data for various elements from batch and column leach tests |

# The case of fly ash from Jönköping

- Classified as non-hazardous waste
- => OK for the landfilling in question
- But the leach rate for lead almost 100 times higher than the leach limit – if it would have applied
- Everything that is legal is not appropriate

- What to do? (Appart from having a good communication with the Authority)

# “Equilibrium conditions”

- Actually, ash ages and reacts when contacted with constituents of air (water, oxygen and carbon dioxide)
- According to the standards; the leach tests are not applicable for waste that reacts with water
- Legislation on acceptance states that “equilibrium conditions” should be sought when leach tests are to be carried out

# Legal and research questions

| | |
|---|---|
| Legal question | Would the leaching of lead reduce to "appropriate" levels if testing were done under more equilibrium-like conditions? |
| Research questions | How would contact with moisture and air for a prolonged time influence the leaching of lead? |
| | Associated question:<br>How would such ageing influence the leaching of chlorides? |

# Scope

- Information search
  - Major elements
  - Minor elements with ionic radii similar to iron
  - Lead
  - Chlorine
- Experiments
  - Laboratory scale batch tests
  - Laboratory scale column tests
  - Pilot scale tests
- Analysis - discussion and conclusions

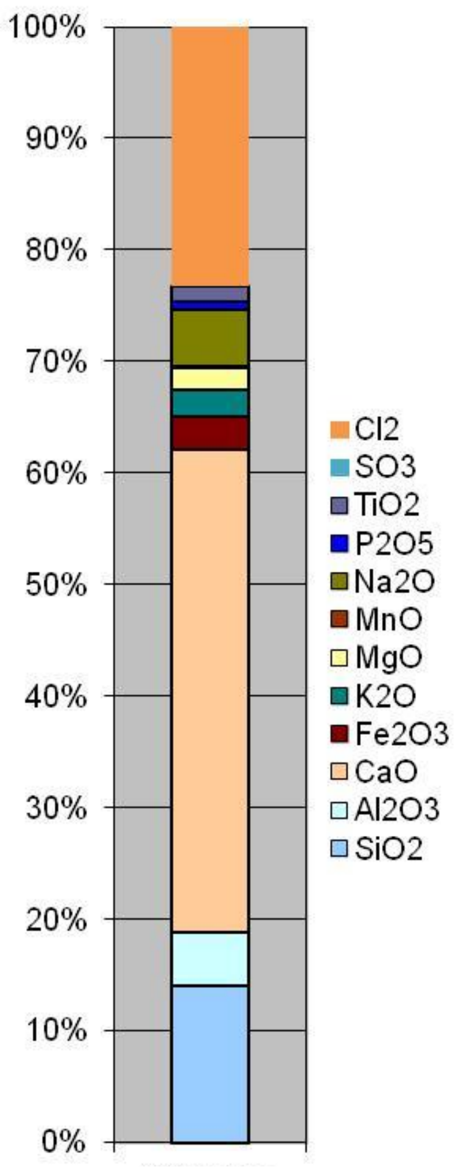
*Example of analysis of trace elements in fly ash from Jönköping Energi AB, ppm by dry weight.*

| **Ämne** | **Fly ash** |
|---|---|
| antimony | 757 |
| arsenic | 50 |
| barium | 1050 |
| lead | 1950 |
| cobalt | 12.1 |
| copper | 630 |
| chromium | 229 |
| molybdenum | 13.1 |
| nickel | 54.1 |
| vanadium | 27.7 |
| tungsten | 10,1 |
| zinc | 8620 |
| cadmium | 83.1 |
| mercury | 8.02 |

*Example of analysis of major elements in fly ash from Jönköping Energi AB, ppm by dry weight.*

| **Figured as** | **Fly ash** |
|---|---|
| Dry content | 68.1 |
| $SiO_2$ | 10.3 |
| $Al_2O_3$ | 3.52 |
| CaO | 31.7 |
| $Fe_2O_3$ | 2.1 |
| $K_2O$ | 1.81 |
| MgO | 1.46 |
| MnO | 0.0947 |
| $Na_2O$ | 3.7 |
| $P_2O_5$ | 0.539 |
| $TiO_2$ | 1.03 |

Major elements



*Example of relative proportions of the major elements in fly ash from Jönköping Energi AB.*

# Phases in ash after maturation ≠ from those formed in the furnace

*Table 3. Minerals phases identified in incinerator ash after ageing [24]. Less abundant phases are labelled with italic fonts.*

| | | | |
|---|---|---|---|
| **Silicate** | | **Oxide** | |
| Melilite | $(Ca,Na)_{2(}Al,Mg)(Si,AL)_2O_7$ | Hematite | $Fe_2O_3$ |
| Wollastonite | $CaSiO_3$ | Magnetite | $Fe_3O_4$ |
| Clinopyroxene | $(Ca,Na)(Fe,Mg,Al)(Si,Al)_2O_6$ | **Carbonate** | |
| Plagioclas | $(Ca,Na)Al(Al,Si)Si_2O_8$ | Calcite | $CaCO_3$ |
| K-Feldspar | $(K,Na)(AlSi_3O_8)$ | | |
| *Biotite* | $K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2$ | **Hydroxide** | |
| *Muscovite* | $KAl_2Si_3Al)O_{10}(OH,F)_2$ | Portlandite | $Ca(OH)_2$ |
| *Montmorillonite* | $(Na,Ca)_{0,3}(Al,Mg)_2SiO_{10}(OH)_2\cdot nH_2O$ | *Goethite* | $FeO(OH)$ |
| **Hydrate** | | *Boemite* | $AlO(OH)$ |
| Hydrocalumite | $Ca_2Al(OH)_6[Cl_{1-x}(OH)_x]\cdot 3H_2O$ | *Gibbsite* | $Al(OH)_3$ |
| Hydrated Gehlenite | $Ca_2Al_2SiO_7\cdot 2H_2O$ | **Phosphate** | |
| **Sulphate** | | Apatite | $Ca(PO4)_3$ $(Cl,F,OH)$ |
| *Anhydrite* | $CaSO_4$ | | |
| *Ettringite* | $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$ | | |
| *Gypsum* | $CaSO_4\cdot 2H_2O$ | | |

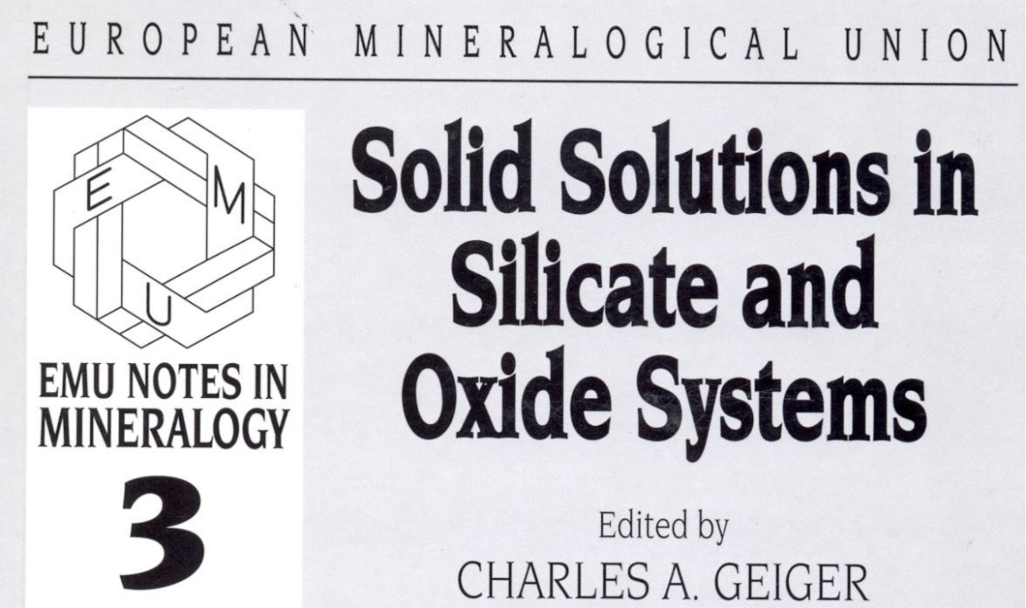
# Often assumed

- That minor elements form phases similarly to the major elements
- I. e. phases in low abundance, but in which the minor elements are major elements

# Why?

- Difficult to “see” phases that occur in low abundance using existing instrumentation
- Commercially available computer codes for thermodynamical calculations do not include solid solution
- Obstacles against interdisciplinary communication

# Well-known among mineralogists e t c since decades



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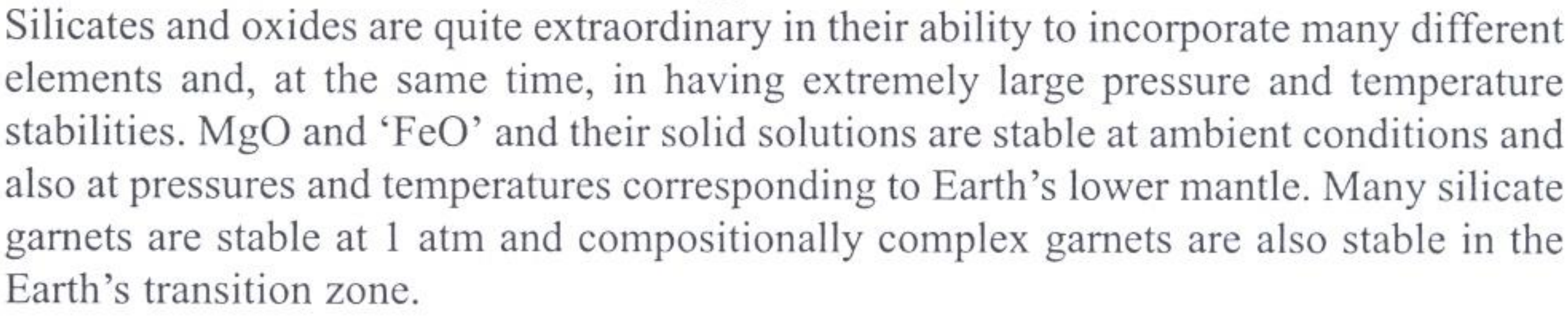
**EMU NOTES IN MINERALOGY**

**3**

**Solid Solutions in Silicate and Oxide Systems**

Edited by
CHARLES A. GEIGER

Minor elements are dispersed – atom by atom – in the phases formed by the major elements



Silicates and oxides are quite extraordinary in their ability to incorporate many different elements and, at the same time, in having extremely large pressure and temperature stabilities. MgO and 'FeO' and their solid solutions are stable at ambient conditions and also at pressures and temperatures corresponding to Earth's lower mantle. Many silicate garnets are stable at 1 atm and compositionally complex garnets are also stable in the Earth's transition zone.

# Ionic radii for trace elements and some other elements, Angstrom / Ångström

| Ox no | I | II | | III | | IV |
|---|---|---|---|---|---|---|
| Spin | | low | high | low | high | |
| Na | 1,02 | | | | | |
| K | 1,38 | | | | | |
| Mg | | 0,72 | | | | |
| Ca | | 1,00 | | | | |
| Al | | | | 0,53 | | |
| Ti | | 0,86* | | 0,67* | | 0,61 |
| V | | 0,79 | | 0,64 | | 0,63 |
| Cr | | 0,73 | 0,82 | 0,62 | | |
| Mn | | 0,67 | 0,82 | 0,58 | 0,65 | |
| Fe | | 0,61 | 0,77 | 0,55 | 0,65 | |
| Co | | 0,65 | 0,74 | 0,53 | 0,61 | |
| Ni | | 0,70 | | 0,56 | 0,60 | |
| Cu | | 0,73 | | | | |
| Zn | | 0,75 | | | | |
| Mo | | | | | | 0,70 |
| Cd | | 0,95 | | | | |
| As | | | | 0,58 | | |
| Sb | | | | 0,76 | | |
| Pb | | 1,18 | | | | |
| Cs | 1,70 | | | | | |
| Ba | | 1,36 | | | | |

* unusual oxidation number

# Goldsmith’s rules

- Difference in ionic radius </≈ 15 %
- Difference in charge ≤ 1 unit
- Moderate difference in electronegativity

- => Cr, Ni, Cu, Zn ⬄ solid solution with Fe-rich phases
- => ≈ as inaccessible as Fe
- But what about Pb and Cl?

<table>
<tr><th>Ox no</th><th>I</th><th colspan="2">II</th><th colspan="2">III</th><th>IV</th></tr>
<tr><th>Spin</th><th></th><th>low</th><th>high</th><th>low</th><th>high</th><th></th></tr>
<tr><td>Na</td><td>1,02</td><td colspan="2"></td><td colspan="2"></td><td></td></tr>
<tr><td>K</td><td>1,38</td><td colspan="2"></td><td colspan="2"></td><td></td></tr>
<tr><td>Mg</td><td></td><td colspan="2">0,72</td><td colspan="2"></td><td></td></tr>
<tr><td>Ca</td><td></td><td colspan="2">1,00</td><td colspan="2"></td><td></td></tr>
<tr><td>Al</td><td></td><td colspan="2"></td><td colspan="2">0,53</td><td></td></tr>
<tr><td>Ti</td><td></td><td colspan="2">0,86*</td><td colspan="2">0,67*</td><td>0,61</td></tr>
<tr><td>V</td><td></td><td colspan="2">0,79</td><td colspan="2">0,64</td><td>0,63</td></tr>
<tr><td>Cr</td><td></td><td>0,73</td><td>0,82</td><td colspan="2">0,62</td><td></td></tr>
<tr><td>Mn</td><td></td><td>0,67</td><td>0,82</td><td>0,58</td><td>0,65</td><td></td></tr>
<tr><td>Fe</td><td></td><td>0,61</td><td>0,77</td><td>0,55</td><td>0,65</td><td></td></tr>
<tr><td>Co</td><td></td><td>0,65</td><td>0,74</td><td>0,53</td><td>0,61</td><td></td></tr>
<tr><td>Ni</td><td></td><td colspan="2">0,70</td><td>0,56</td><td>0,60</td><td></td></tr>
<tr><td>Cu</td><td></td><td colspan="2">0,73</td><td colspan="2"></td><td></td></tr>
<tr><td>Zn</td><td></td><td colspan="2">0,75</td><td colspan="2"></td><td></td></tr>
<tr><td>Mo</td><td></td><td colspan="2"></td><td colspan="2"></td><td>0,70</td></tr>
<tr><td>Cd</td><td></td><td colspan="2">0,95</td><td colspan="2"></td><td></td></tr>
<tr><td>As</td><td></td><td colspan="2"></td><td colspan="2">0,58</td><td></td></tr>
<tr><td>Sb</td><td></td><td colspan="2"></td><td colspan="2">0,76</td><td></td></tr>
<tr><td>Pb</td><td></td><td colspan="2">1,18</td><td colspan="2"></td><td></td></tr>
<tr><td>Cs</td><td>1,70</td><td colspan="2"></td><td colspan="2"></td><td></td></tr>
<tr><td>Ba</td><td></td><td colspan="2">1,36</td><td colspan="2"></td><td></td></tr>
</table>

* unusual oxidation number

# Ionic radii for trace elements and some other elements, Angstrom / Ångström

For Pb ⬄ details in the chemical structures

# Prerequisites for packing

## oxygen = large, cationic element = small

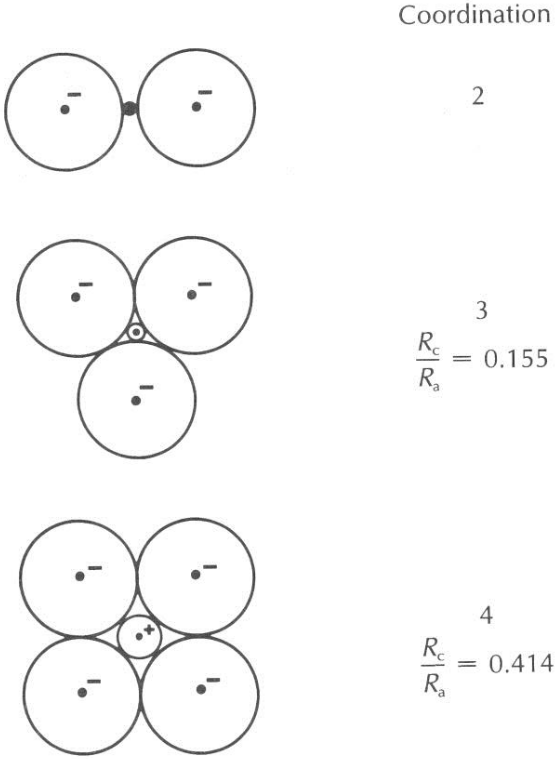
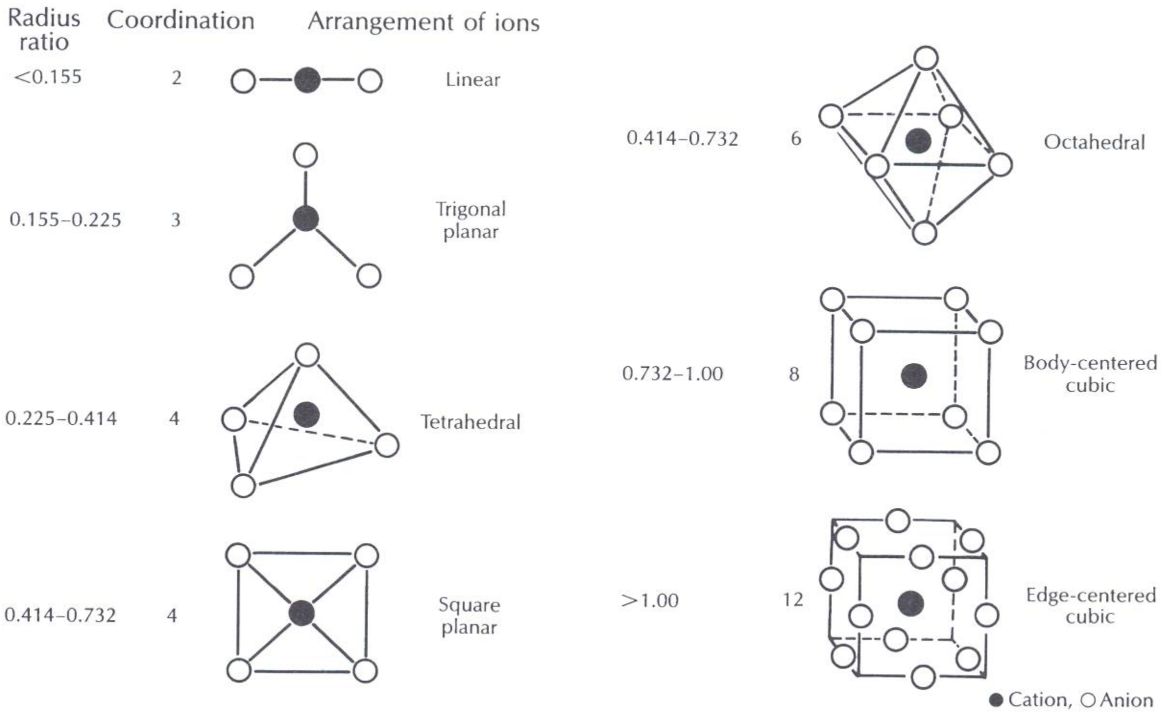


**Figure 7.2** Examples of closest packing of anions around cations at increasing values of the radius ratio. When $R_c/R_a > 0.155$, three anions fit around the cation and when $R_c/R_a > 0.414$, fourfold coordination occurs. Coordination numbers 6, 8, and 12 are also important in mineral structures and are pictured in Figure 7.4.



| Radius ratio | Coordination | Arrangement of ions |
|---|---|---|
| <0.155 | 2 | Linear |
| 0.155–0.225 | 3 | Trigonal planar |
| 0.225–0.414 | 4 | Tetrahedral |
| 0.414–0.732 | 4 | Square planar |
| 0.414–0.732 | 6 | Octahedral |
| 0.732–1.00 | 8 | Body-centered cubic |
| >1.00 | 12 | Edge-centered cubic |

● Cation, ○ Anion

**Figure 7.4** Possible arrangements of ions in crystals for limiting values of the radius ratios and different values of the coordination number.

# Calcite and aragonite, both = $CaCO_3$

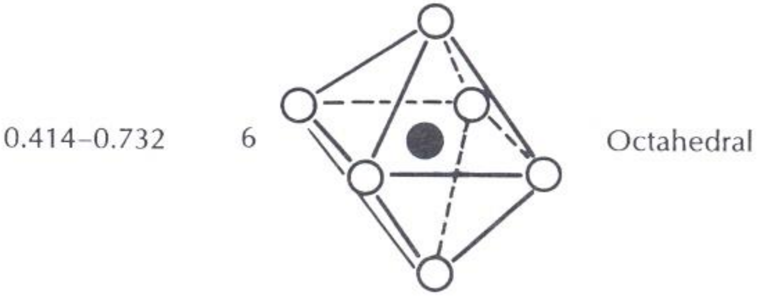
**Calcite**

6-fold co-ordination

Small position

Substitution with:

Fe, Mg, Cr, Ni, Cu, Zn



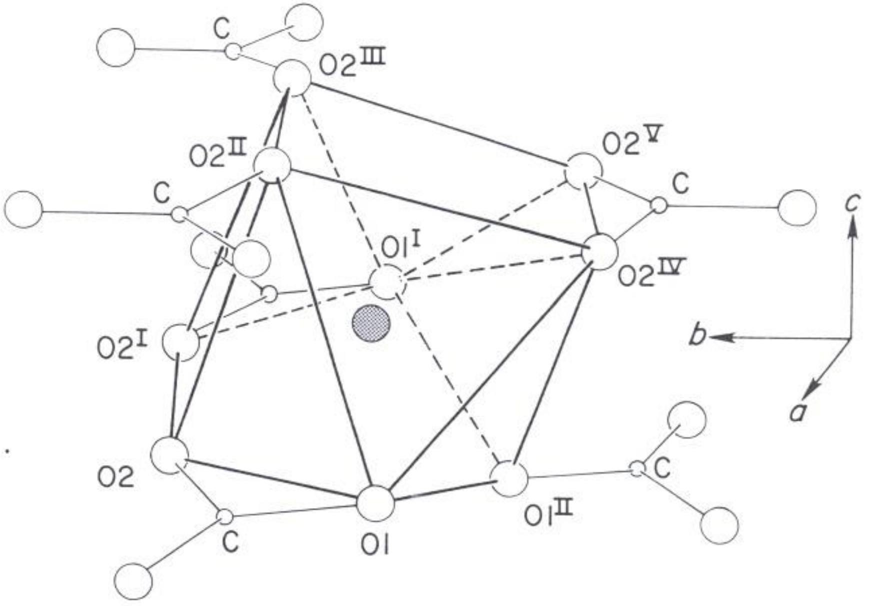
**Aragonite**

9-fold co-ordination

Large position

Substitution with:

Ba, Sr, Pb



# Aragonite structure, stereoscopic view

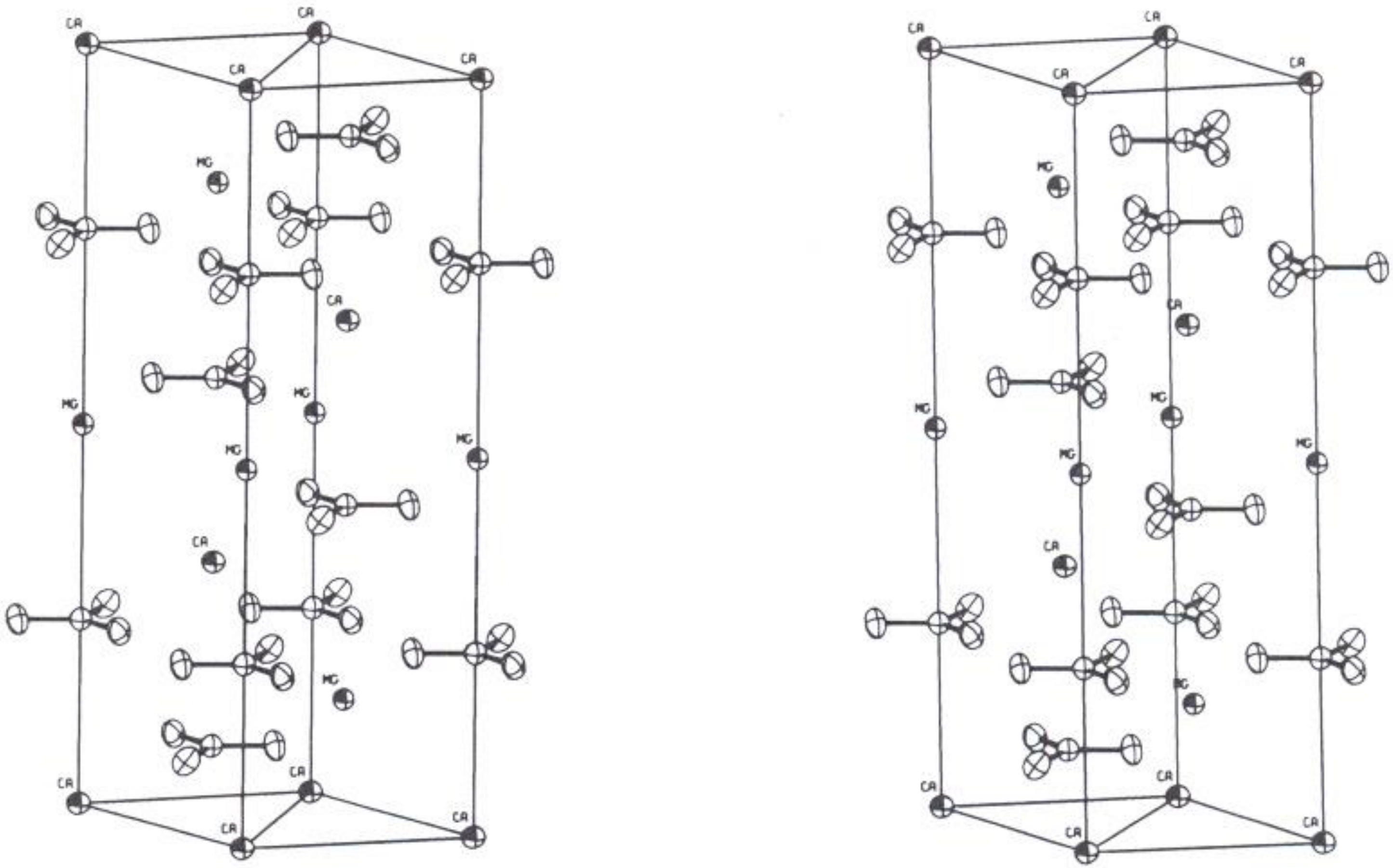


Figure 20. Stereoscopic projection of the hexgonal unit cell for dolomite ($a$ = 4.81 Å, $c$ = 16.00 Å), prepared using the program ORTEP (Johnson, 1965). $c$ is vertical; compare with Figure 4 for the disposition of axes. Cation layers occur at intervals of 1/6 $c$; carbonate layers at levels $\pm z_o$, $1/3 \pm z_o$, $2/3 \pm z_o$.

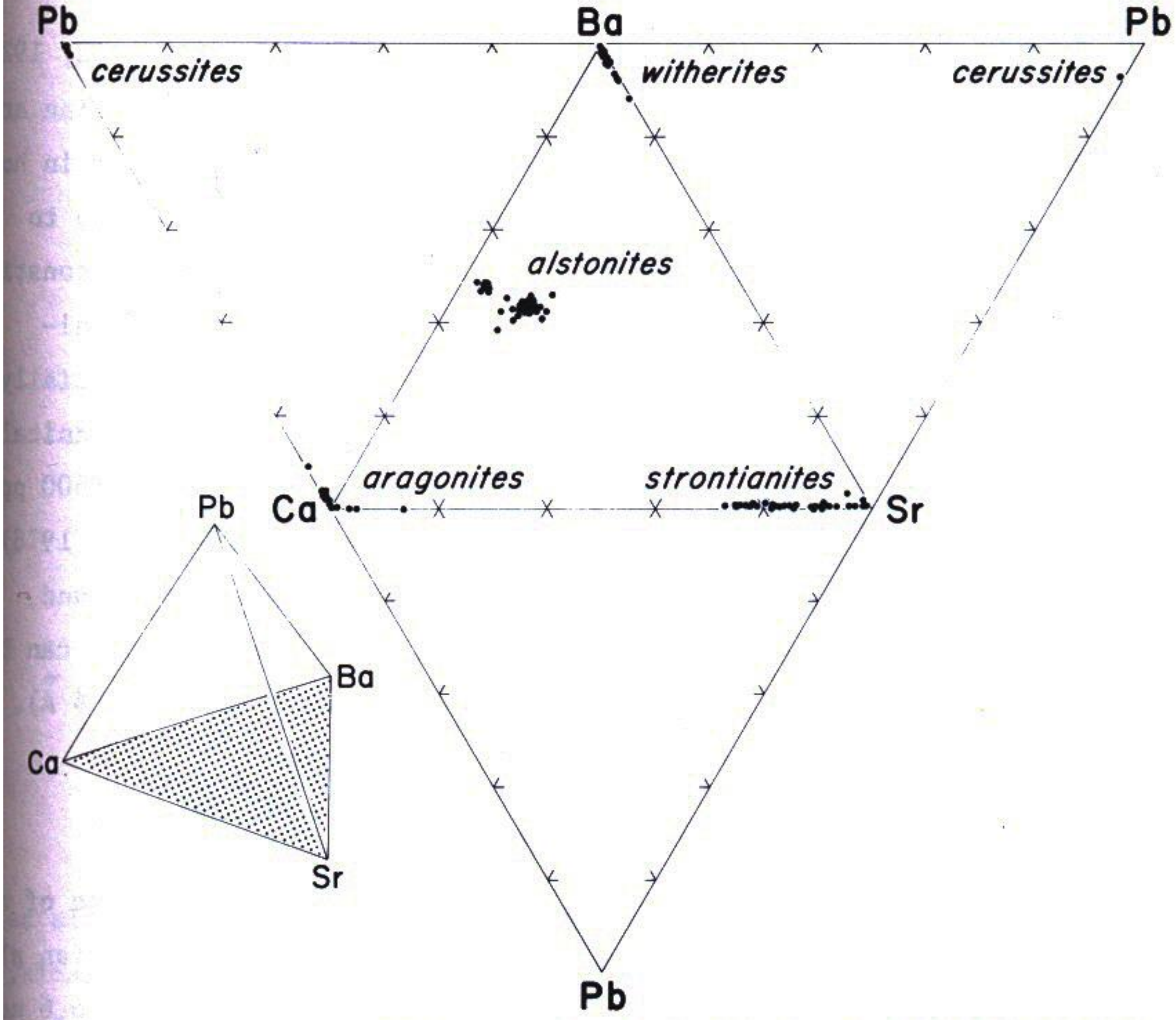


Figure 9. Compositions of 106 inorganic orthorhombic minerals projected onto the faces of the $CaCO_3$-$SrCO_3$-$BaCO_3$-$PbCO_3$ tetrahedron. Data was obtained from

# Chlorine

- Although frequently assumed, not all chlorine may be leached in the form of chloride
- Less soluble phases may form, e. g.
  - $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$, and
  - $3CaO \cdot Fe_2O_3 \cdot CaCl_2 \cdot 10H_2O$
- Both of them are broken down by carbonatation, thus making all chlorine leachable

# Conclusions from the information search

- Exposure to water, oxygen and carbon dioxide in the air will lead to
  - Formation of hydroxides
  - Oxidation
  - Carbonatation
- Fates for the trace elements
  - Remain in original forms, e. g. in soil particles
  - Go into solid solution
  - Form phases in which they are major elements
- Pb may go into solid solution with aragonite
- Cl may become “fully” water soluble

# Considerations for the testing

- Differentiate between hydration, oxidation and carbonatation
- Carbonatation may require:
  - Open pore structures to allow access of the carbon dioxide in the air (0.04 %)
  - Presence of free water to catalyse the carbonatation reaction
- $CaCl_2$ is hygroscopic ⇔ samples may dry out as well as deliquesce during contact with air

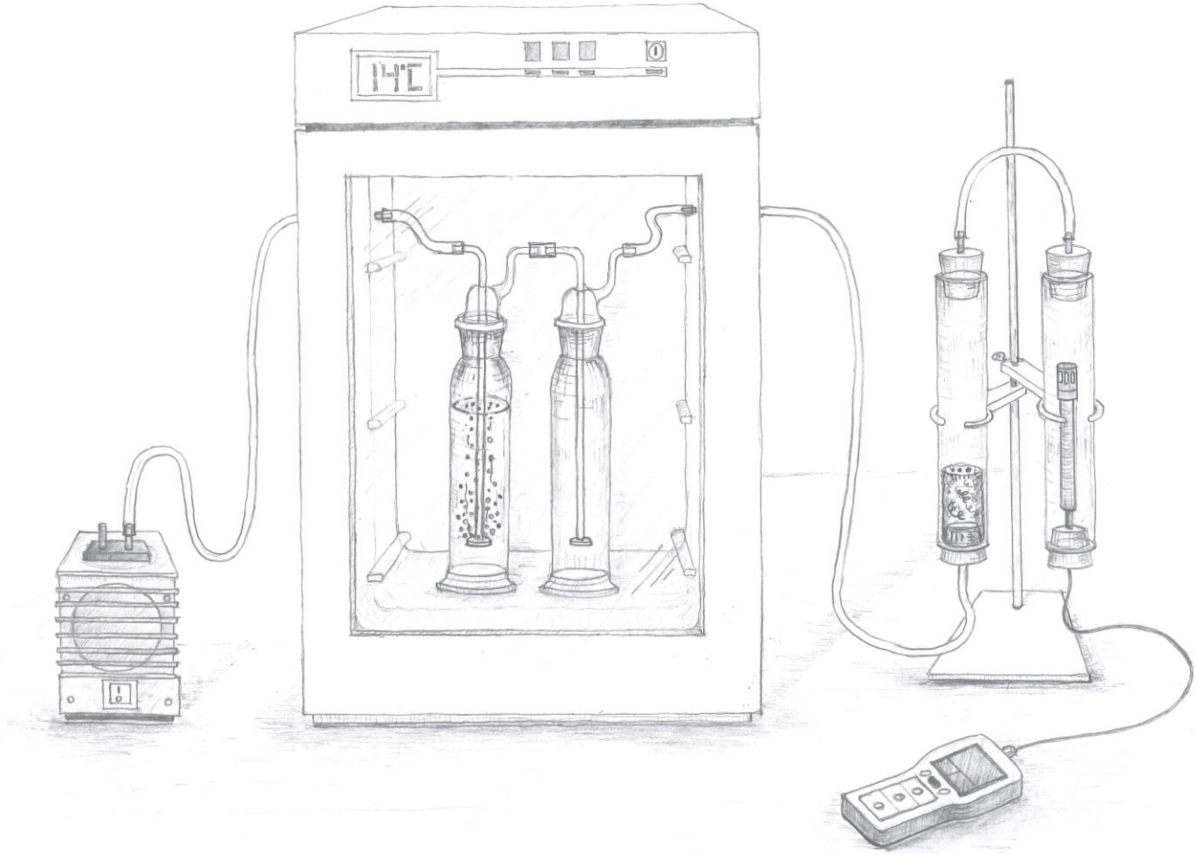
# Batch tests

- Cans with moistened and granulated ash
- Cans subjected to the following variations
  - Moisture
  - Time
  - Access to air
    - None
    - Intermittently to allow essentially only oxygen
    - All the time to facilitate carbonatation
- Batch leaching & chemical analysis of leachant

# Batch tests, results

- Moderate reduction in Pb leaching on contact with only moisture and oxygen
- Moderate sensitivity with regard to moisture content
- Leaching of Pb decreased monotonously over a period of months for samples with full access of air
- Good basis for column tests

# Column test



- Moistened and granulated ash
- In a column exposed to a flow of air
- Air being bubbled through water at a temperature lower than the ambient
- Upper and lower half of column subjected to batch leaching & chemical analysis of leachant

# Results of column test

- Leaching of Pb decreased by almost three orders of magnitude in comparison with fresh ash
- Leaching of Sb increased by somewhat more than one order of magnitude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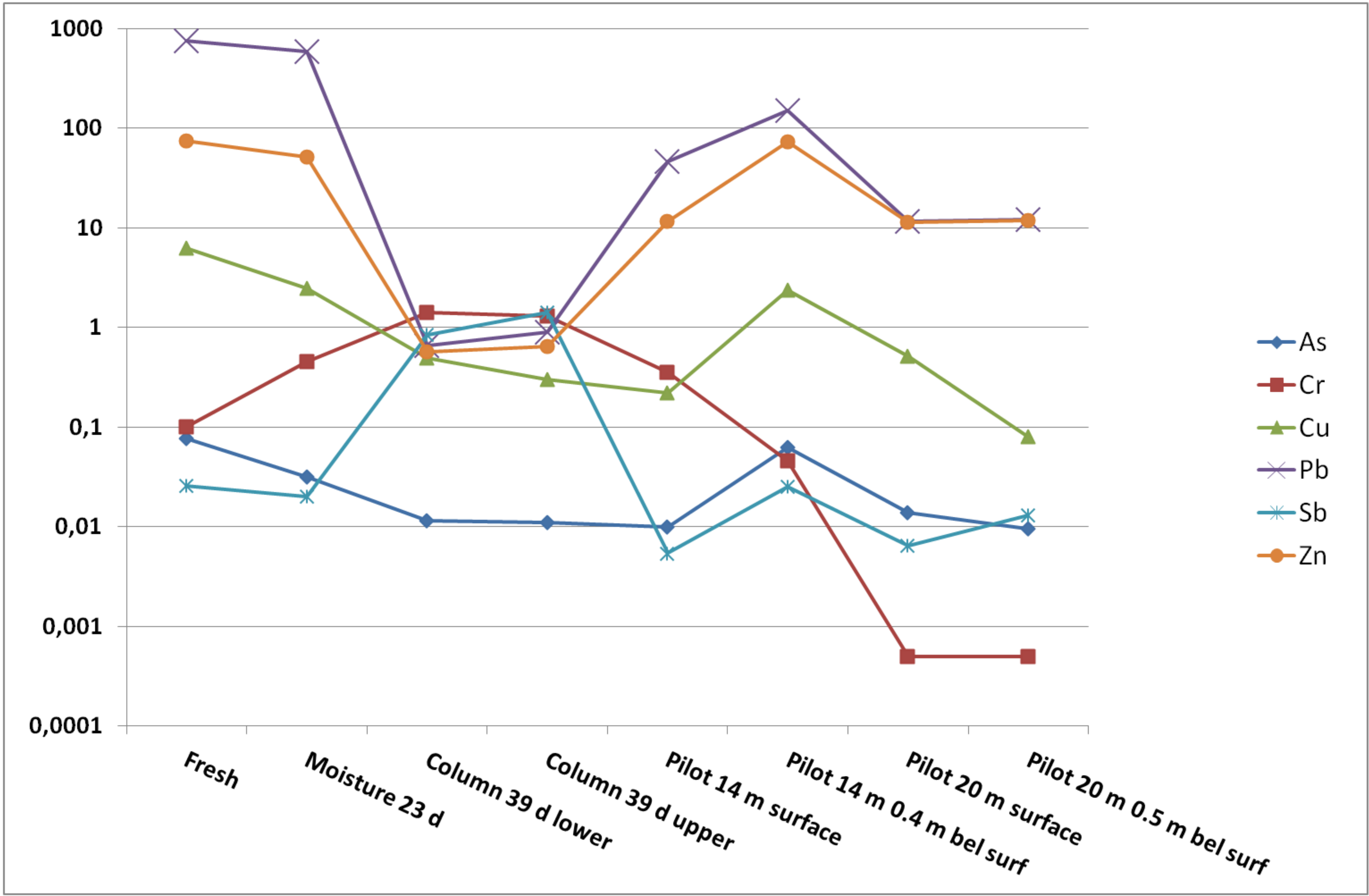
# Results of pilot scale test

- Leaching of Pb decreased by almost two orders of magnitude in comparison with fresh ash
- Leaching of Sb did not increase

# Some selected leach data, mg/kg



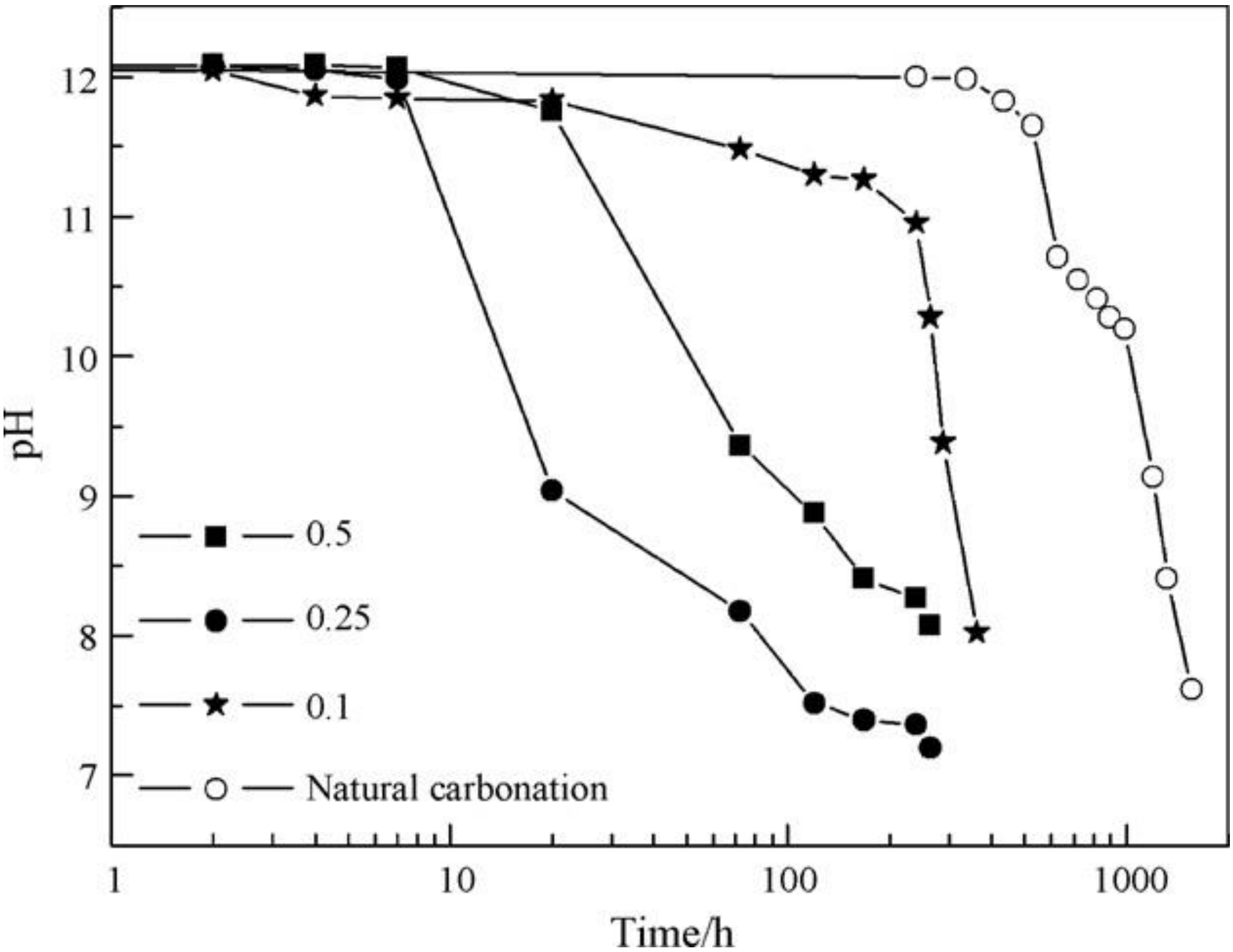
# Conclusions: Literature search Pb

- Forms of occurrence for Pb:
  - Metastable high temperature form
  - Solid solution
  - Minor phases in which Pb is a major element
- Solid solution may be favoured in relation to “minor phase” <= aragonite structure
- A likely explanation is that it follows calcium from e. g. $CaCl(OH)$ to $CaCO_3$
- Simultaneously, all Cl becomes readily susceptible to leaching

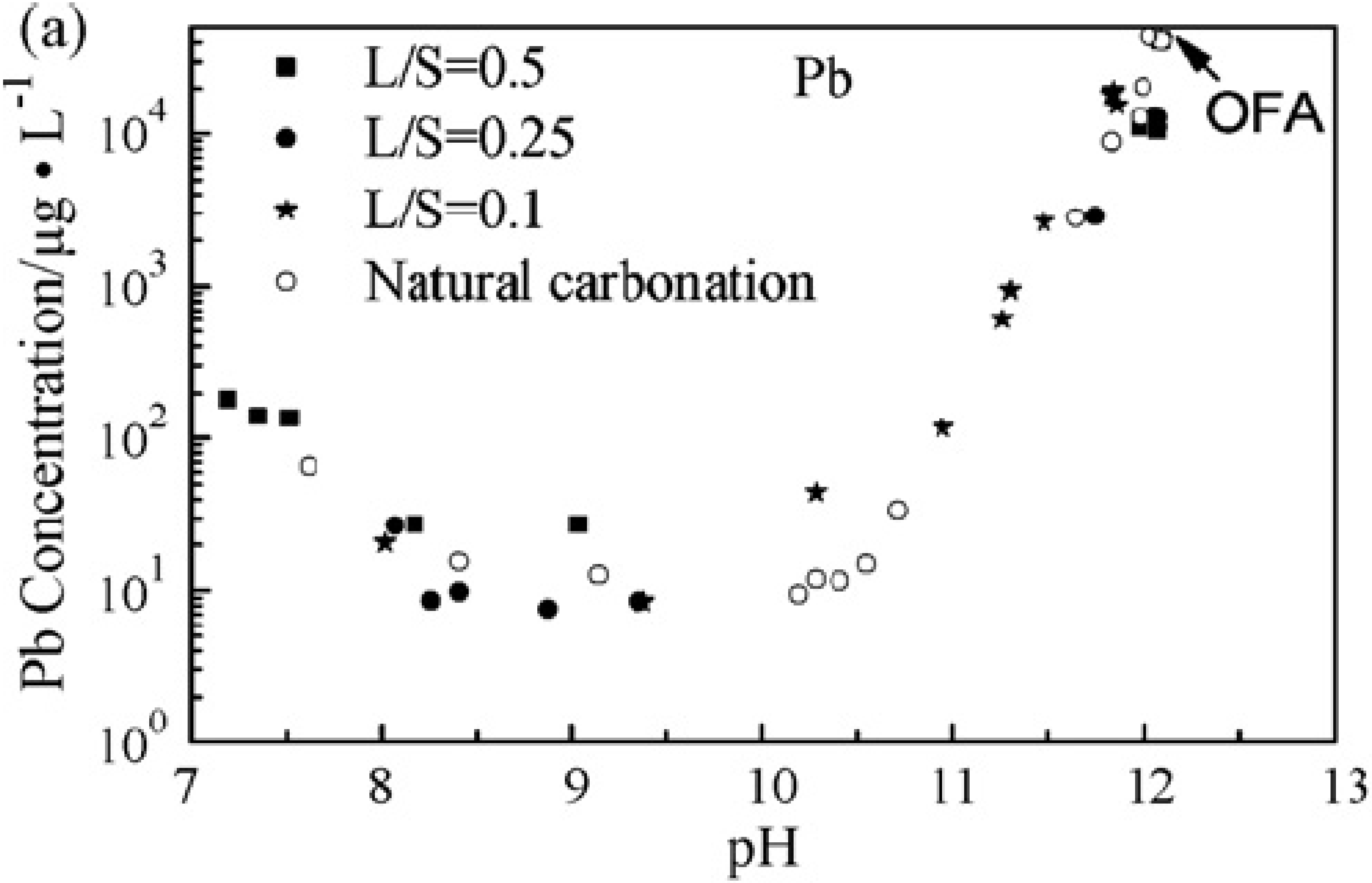
# Conclusions experiments

- Pb leaching decreases to low levels on carbonation
- The leaching of Sb incleases
- Findings in agreement with data from China published during the course of the work

# Carbonatation in air – Chinese study



# Carbonatation in air – Chinese study, contd.



# Industrial processes for carbonatation

- A chemical process is in operation in South Korea
- A chemical process is presently being developed in Norway
- In situ carbonatation practiced for decades on a very large scale in the bentonite industry

# “Farming” at American Colloids Co in Wyoming

# In conclusion

- Support for stabilisation of lead through carbonatation
- => landfilling at a site for non-hazardous waste
  - Not only in compliance with the legislation
  - But also appropriate
- Carbonatation in situ may well be preferable to that in a chemical process plant