## APPENDIX A:
## A BRIEF NOTE ON THE CHEMICAL AND GEOCHEMICAL CLASSIFICATION OF THE ELEMENTS

**LITHOPHILE** elements are enriched in the silicate crust of the earth (Goldschmidt, 1937, 1954) which, by volume, is made up mainly of oxygen; this list includes Li, Be, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Rb, Sr, Y, Zr, Nb, Cs, Ba, REE, Hf, Ta, W, Th, U (please note that, independently of V.M. Goldschmidt, a geochemist, R.G. Pearson, a chemist, realized that these elements, when they form complexes in solution, have an affinity toward oxygen-containing ligands).

Of this list of lithophile elements, some elements will become mobilized during chemical weathering (i.e. will be released to the soil solution, and from here to rivers, lakes, and groundwaters) because their low formal oxidation states (+1, +2) allows them to remain dissolved in aqueous solution: Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba.

Exceptions

Uranium is an exception in that it can be very mobile in oxygenated environments, because its formal oxidation state (+6) is so high that it forms anionic species which are quite soluble. For the same reason, this may also be true of As, Mo, W, and Re which form the arsenate, molybdate, tungstate and rhenate anions (Pourbaix, 1966). In our reference water from the Elmvale Groundwater Observatory, these elements are enriched in groundwater, relative to rainwater (Shotyk et al., 2010).

Other lithophile elements behave conservatively during chemical weathering (i.e. they will become residually enriched in soils), either because they are hosted in extremely stable minerals (such as rutile or zircon), or because they will rapidly hydrolyze in aqueous solution due to their high formal oxidation state (+3, +4) and precipitate as insoluble hydroxides: Al, Si, Sc, Ti, V, Cr, Y, Zr, Nb, REE, Hf, Ta, W, Th.
Exception: $Si^{4+}$ is not stable in aqueous solution. In natural waters, Si is found almost exclusively in the form of silicic acid, $H_4SiO_4$: this is supplied mainly from the weathering of feldspars and micas, very little from quartz (as it is so stable).
Exceptions: Fe and Mn are *immobile in oxidizing environments* because in their +3 and +4 oxidation states they form insoluble oxides and hydroxides; they are *mobilized under reducing (anoxic) conditions* because in their +2 oxidation states they do not form hydroxides except under extremely alkaline conditions.

For a better understanding of the behaviour of the elements in respect to chemical weathering, the chapter by Chesworth (1992) is recommended.

Of the list of mobile lithophile elements (Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba), only Mg, K and Ca are essential for plants; these plus Na are essential for animals; all the others (Li, Be, Rb, Sr, Cs, Ba) are considered "non-critical" for life as they are relatively mobile (so they will not accumulate in soils) and are not especially toxic.

Of the list of immobile lithophile elements (Al, Si, Sc, Ti, V, Cr, Y, Zr, Nb, REE, Hf, Ta, W, Th), none are essential for plants and only Si and Cr are essential for animals. Because this list of elements (Al, Si, Sc, Ti, V, Cr, Y, Zr, Nb, REE, Hf, Ta, W, Th) is found almost exclusively in insoluble solids, in the atmosphere they are also found in the form of insoluble mineral particles, derived from wind erosion of soils, can be used as indicators of the amount of mineral matter in our samples (moss, peat, snow).

**CHALCOPHILE** (sulphur-loving) elements are enriched in sulphide minerals (Goldschmidt, 1937, 1954), while their abundance in the Earth's Crust is low (Dutch, 1999): Ag, As, Bi, Cd, Hg, Pb, Sb, Se, Te, Tl
(please note that, once again, independently of V.M. Goldschmidt, R.G. Pearson realized that these elements, when they form complexes in solution, have an affinity toward sulphur-containing ligands). These elements are mobilized to the environment from human activities such as mining, smelting, and refining of base metals (Cu, Ni, Zn, Pb,,,). These elements are also enriched in coal (because coal commonly contains inclusions of sulphide minerals which form in coal-forming environments such as swamps), so these elements are also emitted to the environment from coal combustion.

**SIDEROPHILE** elements are those which are enriched in the Earth's core which is essentially an alloy of Fe and Ni; Goldschmidt figured this out by analyzing iron meteorites. This list, in addition to Fe and Ni (and Co), includes the Platinum Group Elements: Ru, Rh, Pd, Os, Ir, Pt. These are more or less irrelevant to life on earth because the abundance of these elements in the Earth's Crust is so low (all below one part per billion in the UCC) and because they are so insoluble. The composition of meteorites reflects the composition of the bulk earth before it differentiated into crust, mantle, and core and, given the low abundance of siderophile elements in the crust, Goldschmidt realized that they must be highly enriched in the earth's core.

**ATMOPHILE** elements are those which are found mainly in air (e.g. the noble gases).

**BIOPHILE** elements are those which are either essential to living organisms, namely

- plants (B, Mg, K, P, S, Cl, Ca, Mn, Fe, Ni, Cu, Zn, Mo) or
- animals (F, Na, Mg, Si, P, S, Cl, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo, Sn, I)

**FIGURE 1:** Goldschmidt's Geochemical Classification of the Elements

**FIGURE 2:** Abundance of the elements in the earth's crust (Dutch, 1999).

**FURTHER READING**

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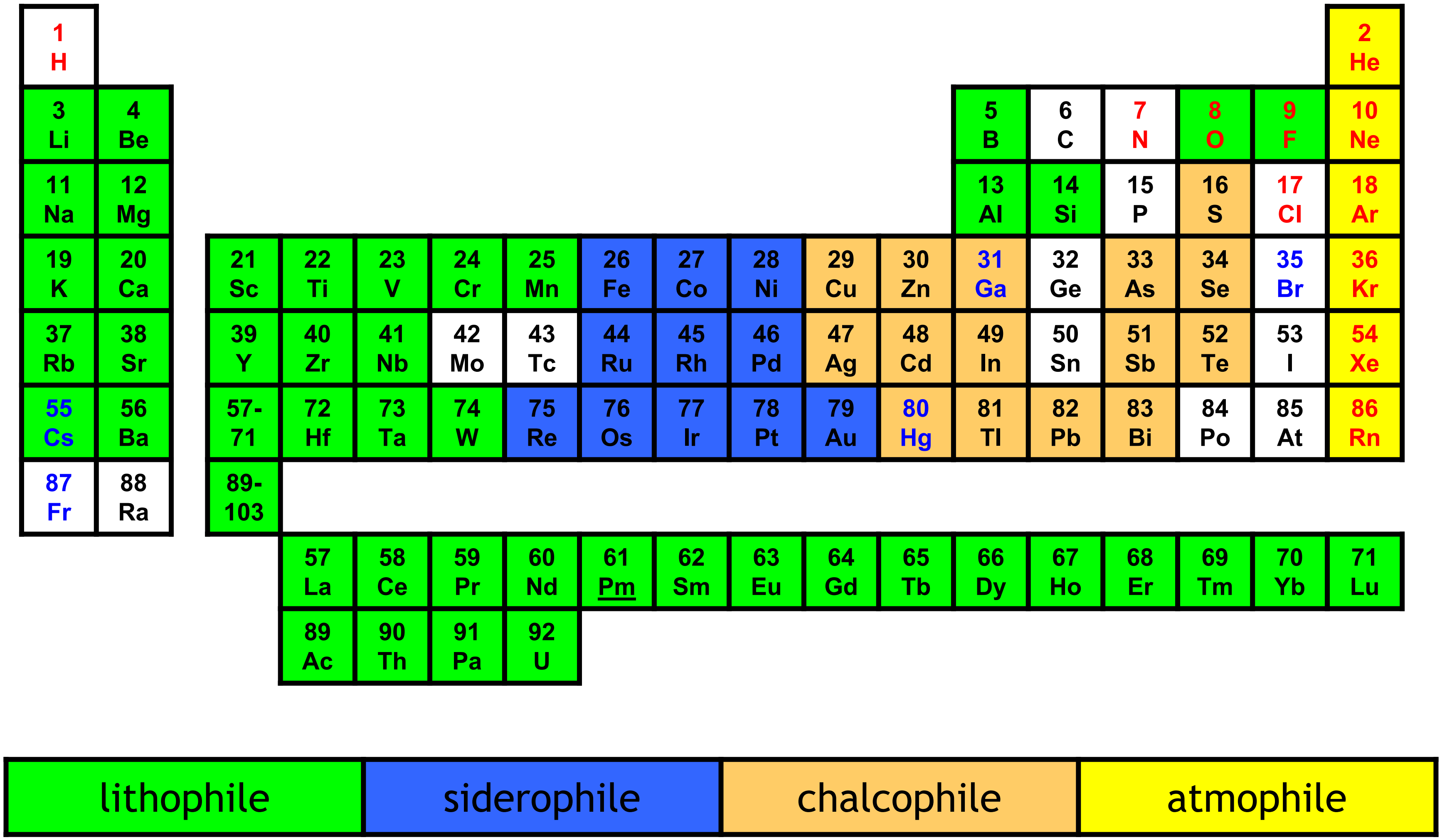
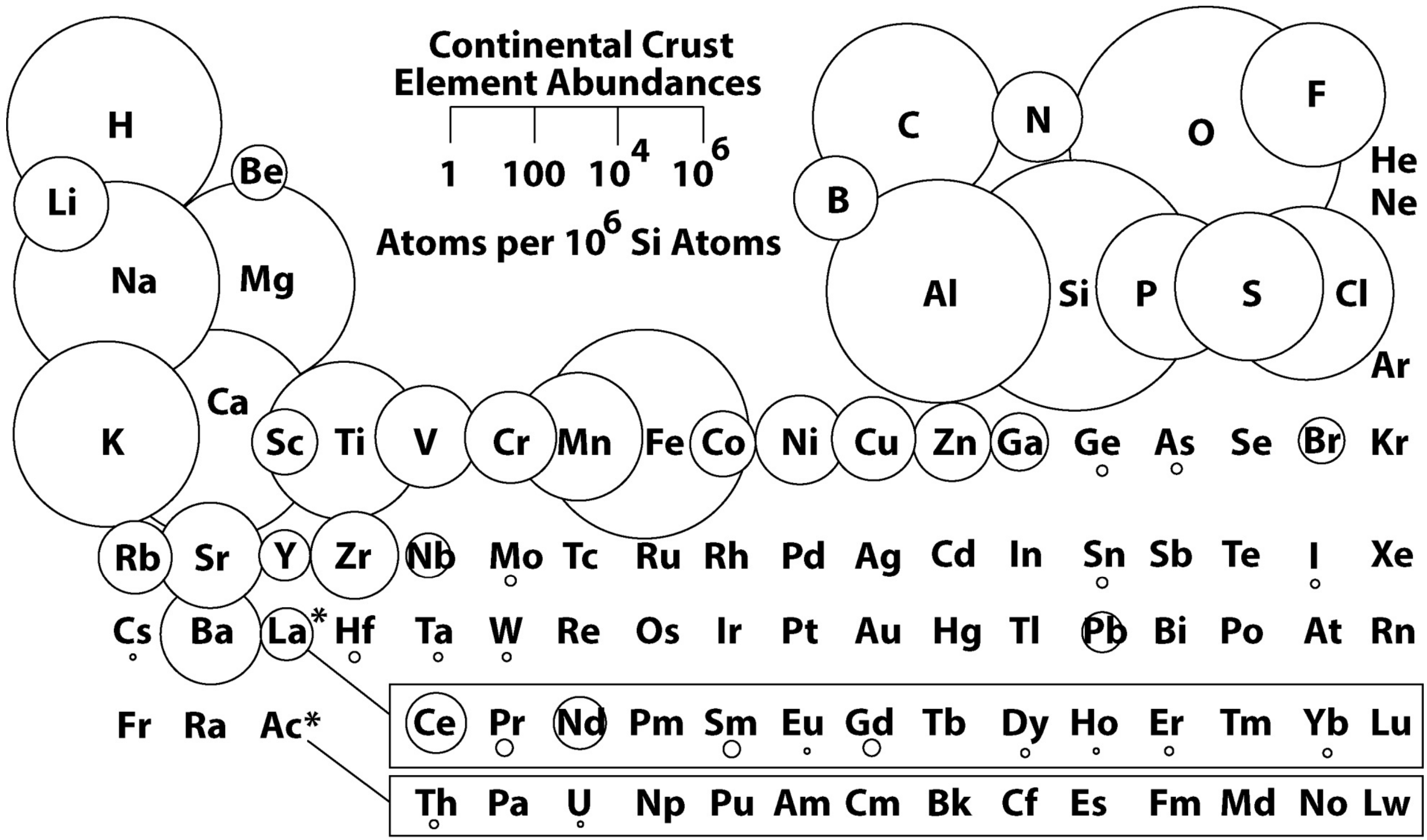
# GOLDSCHMIDT`S GEOCHEMICAL CLASSIFICATION OF THE ELEMENTS




Shotyk, Trace elements in the Athabasca Bituminous Sands. Facts and Misconceptions
**APPENDIX I, Figure 1**




Shotyk, Trace elements in the Athabasca Bituminous Sands. Facts and Misconceptions

**APPENDIX I, Figure 2**