

## Trace Element Geochemistry

### Lecture 1

#### **A. Beginnings of Geochemistry:**

The field of Geochemistry slowly emerged along with the development of Geology in 1700 and 1800's (James Hutton, 1726-1797, is known as the "Father of Geology"). Physical Chemistry and Geology were effectively combined by establishment in 1907 of the Geophysical Laboratory of the Carnegie Institute of Washington. N.L. Bowen, a MIT-trained scientist, published "The Evolution of the Igneous Rocks (1928),

V.M. Goldschmidt (1888-1947) is known as the father of Modern Geochemistry, (see Geochemical Society Spec. Pub. No. 4 by B. Mason (1992) for a biography of Goldschmidt). His collected efforts are summarized in the book "Geochemistry", Clarendon Press, Oxford, 1954.

#### **B. Definition of Trace Elements:**

There is no rigorous definition of a trace element, but typically 11 elements are described as major elements because they form more than 99 wt% of most igneous rocks; the relative abundance of major elements determines the proportions of rock-forming minerals such as feldspar, quartz, micas, olivine, pyroxenes and amphiboles. These major elements (ME) are indicated in the periodic table (Figure 1). They are in order of increasing atomic number O, Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe.

## Periodic Table of the Elements and Ground-State Electronic Configurations

Period	Group →																																																																																																																																																																																																				
1	IA 1 H $1s^1$															2 He $1s^2$																																																																																																																																																																																					
2	3 Li $[He]2s^1$	IIA 4 Be $[He]2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$																																																																																																																																																																																			
3	11 Na $[Ne]3s^1$	12 Mg $[Ne]3s^2$	IIIA	IVA	VA	VIA	VIIA	VIII ←	→	IB	IIB	13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$																																																																																																																																																																																				
4	19 K $[Ar]4s^1$	20 Ca $[Ar]4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$																																																																																																																																																																																			
5	37 Rb $[Kr]5s^1$	38 Sr $[Kr]5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo □ $4d^5 5s^1$	43 Tc $4d^5 5s^1$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$																																																																																																																																																																																			
6	55 Cs $[Xe]6s^1$	56 Ba $[Xe]6s^2$	57 * La $5d^1 6s^2$	72 Hf $5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$																																																																																																																																																																																			
7	87 Fr $[Rn]7s^1$	88 Ra $[Rn]7s^2$	89 † Ac $6d^1 7s^2$	104 Unq	105 Unp	106 Unh	107 Uns																																																																																																																																																																																														
		* 58 Ce $4f^1 5d^1 6s^2$														59 Pr $4f^3 6s^2$														60 Nd $4f^4 6s^2$														61 Pm $4f^5 6s^2$														62 Sm $4f^6 6s^2$														63 Eu $4f^7 6s^2$														64 Gd $4f^7 5d^1 6s^2$														65 Tb $4f^9 6s^2$														66 Dy $4f^{10} 6s^2$														67 Ho $4f^{11} 6s^2$														68 Er $4f^{12} 6s^2$														69 Tm $4f^{13} 6s^2$														70 Yb $4f^{14} 6s^2$														71 Lu $4f^{14} 5d^1 6s^2$													
		† 90 Th $6d^2 7s^2$														91 Pa $5f^2 6d^1 7s^2$														92 U $5f^3 6d^1 7s^2$														93 Np $5f^4 6d^1 7s^2$														94 Pu $5f^6 7s^2$														95 Am $5f^7 7s^2$														96 Cm $5f^7 6d^1 7s^2$														97 Bk $5f^8 6d^1 7s^2$														98 Cf $5f^{10} 7s^2$														99 Es $5f^{11} 7s^2$														100 Fm $5f^{12} 7s^2$														101 Md $5f^{13} 7s^2$														102 No $5f^{14} 7s^2$														103 Lr $5f^{14} 6d^1 7s^2$													

Figure by MIT OpenCourseWare.

Figure 1: Periodic Table – The periodic table of the elements is organized according to electron configuration; that is the systematic arrangement of electrons in orbitals surrounding the nucleus. This table indicates for each element the outermost electrons; these are the electrons that determine the chemical bonds between elements. In order to understand and predict the behavior of a trace element in an igneous system, it is essential to know where the element of interest lies in the periodic table.

Elements that typically occur as major elements (ME) in igneous rocks and minerals are indicated by yellow squares. Note that ME are in the first four periods of the periodic table; all other elements typically occur in lower abundance, <0.1 wt.%, and are described as Trace Elements.

### C. Modern Development of Trace Element Geochemistry:

The origins of this field clearly arise from the efforts of Goldschmidt but full development of the field was hindered by the paucity of precise and accurate abundance data for trace elements in rocks. This hindrance has gradually been removed with development of new analytical techniques. Initially the use of X-ray fluorescence and more recently other analytical techniques such as isotope dilution mass spectrometry, neutron activation analysis and most recently the emergence of inductively coupled plasma mass spectrometry (ICP-MS). In addition, determination of trace element abundances in minerals is now possible through use of techniques which can determine the compositions of small “spots” (10’s of microns) using focused beams, such as the ion microprobe (secondary ion mass spectrometry), or lasers, laser ablation ICP-MS. It is important that a trace element geochemist become familiar with the pros and cons of analytical techniques. A course in Analytical Geochemistry is desirable. This course will not discuss analytical techniques but there are numerous useful books. Two are:

(1) Modern Analytical Geochemistry, edited by R. Gill, Addison Wesley Longman Limited, 1997.

(2) A Handbook of Silicate Rock Analysis, P.J. Potts, Blackie, 1987.

With the acquisition of trace element abundance data sets, a need for theoretical understanding of trace element behavior was needed. Perhaps the first landmark papers in this field are those of Gast (1968, *Geochim. Cosmochim. Acta*, 32, 1957-1986) and Schilling and Winchester (1967, pp. 267-283, In: Mantle of Earth and Terrestrial Planets, Interscience). Models for understanding the behavior of trace elements in mineral-silicate melt systems will be discussed in this course.

#### **D. Sites for Trace Elements (TE) in Minerals (see Figure 2)**

1. Direct substitution of TE into specific structural sites of minerals: e.g.,  $\text{Ni}^{+2}$  in the site that contains  $\text{Mg}^{+2}$  in  $\text{Mg}_2\text{SiO}_4$  (Figure 2b).
2. Defect sites: Minerals do not have perfect arrangement of cations and anions, and there are defect sites such as Schottky defects whereby a vacancy within the lattice is created by transferring an atom from interior of crystal to the surface of the crystal. Another type of vacancy defect is the Frenkel defect whereby an atom is transferred to an interstitial position. These vacancies can be occupied by TE (Figure 2c).
3. Inclusions of a different phase in a host mineral: These may be melt, fluid or solid inclusions trapped within a growing mineral. One way to form such inclusions is exclusion of elements not incorporated in a mineral to the grain boundary surface where the activity of the excluded element may be sufficient to form an accessory phase, such as zircon where the dominant cations are Zr and Si or apatite where the dominant cations are Ca and P (Figure 2d). When inclusions can be recognized there are no problems in data interpretation, but it is likely that some inclusions are too small to readily recognize.
4. Adsorption on surfaces: The surfaces of phases have different bonding characteristics than interiors of phases, so grain boundaries may have different TE concentrations than the interiors (Figure 2d). This can be evaluated by mild acid-leaching of silicate phases with analyses prior to and subsequent to leaching.

In summary, all of these mechanisms for TE incorporation into minerals are important, but the mechanism of direct substitution of TE into a structural site is the only process that is well understood; hence we will emphasize this mechanism. However, we will read and discuss papers focused on Melt Inclusions and the Role of Surfaces in controlling trace element abundances. In Lecture 2 we will consider the thermodynamics of dissolving TE in minerals.

Figure 2: Two dimensional arrays of a structure composed of X and M ions showing possible mechanisms for incorporation of ions of trace element Y.

(a) Pure X-M structure

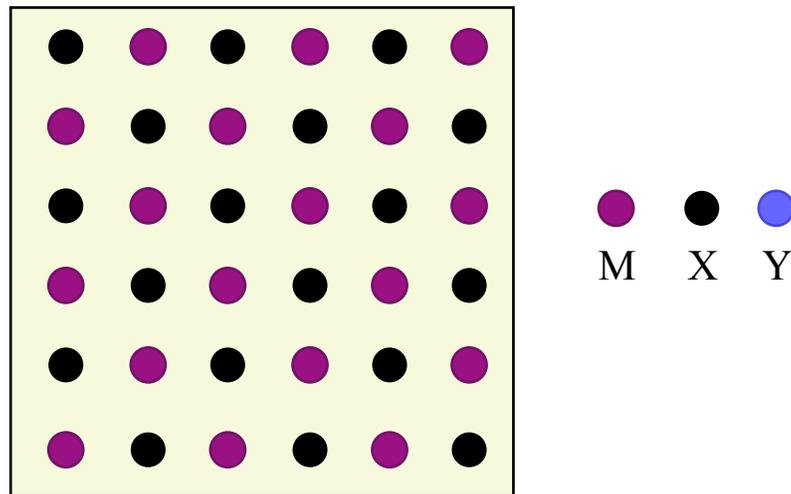


Figure by MIT OpenCourseWare.

(b) XM with incorporation of two ions of element Y at structural sites usually occupied by X ions.

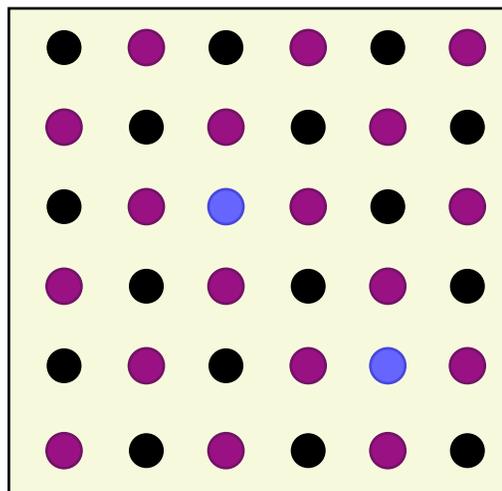


Figure by MIT OpenCourseWare.

- (c) Formation of vacancies that can be occupied by TE.  
 Upper – Schottky defects form when atoms of X and M leave interior sites in the crystal. The vacancies formed, indicated by squares, can be occupied by TE.

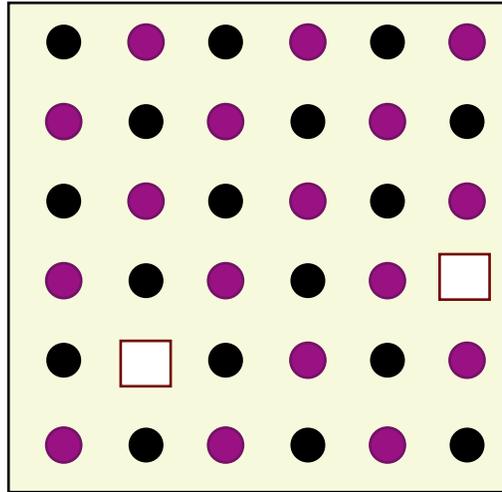


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- Lower – Frenkel defects form when ions of M are transferred to interstitial locations (red circles enclosed in squares) forming vacancies, open squares, that can be occupied by TE.

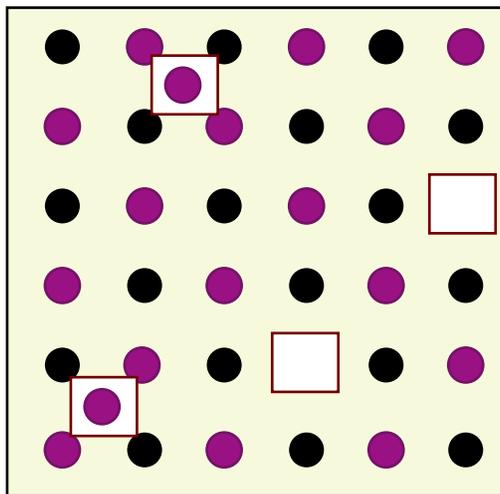


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(d) Inclusion of TE rich zones within a host crystal, e.g., zircon ( $\text{ZrSiO}_4$ ) in biotite.

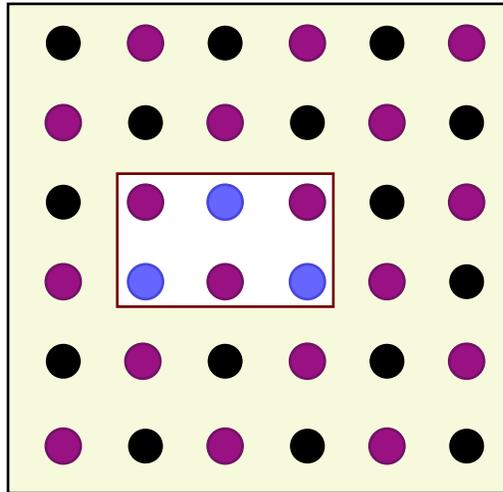


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(e) Absorption of TE on surface of a crystal where bonding differs from that in the crystal interior.

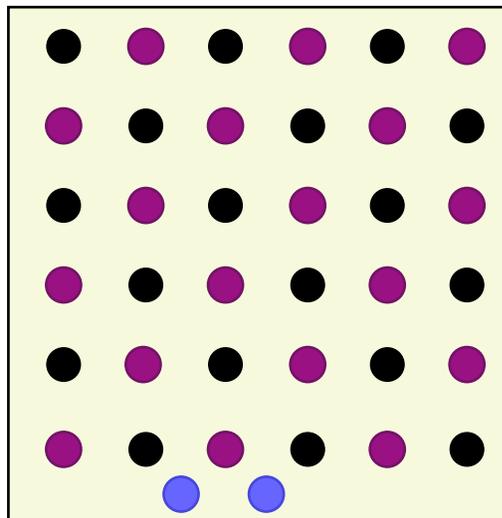


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