SHORT COMMUNICATIONS

LITHOPHILE, CHALCOPHILE, SIDEROPHILE: CAN THESE TERMS BE QUANTIFIED?[1]

R. D. SCHUILING[2]

The terms lithophile, chalcophile and siderophile are commonly used to indicate the geochemical behaviour of elements. Elements which tend to concentrate in the silicate phase are called 'lithophile', those which concentrate in a sulphide phase 'chalcophile', and the elements which stay in the metallic phase 'siderophile'.

It seems logical, therefore, to see whether the Gibbs energies of formation of the first-formed sulphides and oxides of the elements provide a quantitative insight in their geochemical character. This approach has been tried by several authors (see RANKAMA & SAHAMA, 1950), but has met only with limited success. As more thermodynamic data on minerals are now available, we have constructed a plot of Gibbs energies of formation of oxides and sulphides. The procedure was to choose the sulphide and oxide which forms at respectively the lowest sulphur and oxygen fugacity, and to normalize the Gibbs energies to one sulphur or one oxygen. The data were taken mainly from ROBIE ET AL. (1978), GARRELS & CHRIST (1965) and KUBASCHEWSKI & EVANS (1958). In the last mentioned case enthalpies of formation are given, but the difference between enthalpies and Gibbs energies of oxides and sulphides is rather small at room temperature.

The results are given in figure 1. The plot has the advantage that the position of an element is directly related to the oxygen and sulphur pressures at which it forms an oxide, or a sulphide. If we treat the geochemical character of the elements in this way, we say in fact that their character is only determined by their relative affinity for sulphur and oxygen respectively. The boundary between siderophile and lithophile will be parallel to the sulphur fugacity axis (or an equivalent expression), the boundary between siderophile and chalcophile will be parallel to the oxygen fugacity axis, whereas the boundary between chalcophile and lithophile will have a slope of 1, provided that the scale on both axes is the same.

Elements with known lithophile character generally plot in the lithophile field. The correlation between the chalcophile character of elements and the Gibbs energies of formation of their sulphides is poor, as has been noted before by RANKAMA & SAHAMA (1950), who used less complete data which were not normalized. It is somewhat surprising to see that the alkalis fall well within the chalcophile field; this is correct, however, as the alkali elements on their own are chalcophile, as is evident from their behaviour in metallurgical processes (MURTHY & HALL, 1970).

In the real world of geochemistry, however, the alkali elements will not occur separately, but in geochemical environments with excess silica and alumina. As Si and Al are always present in oxide form, K_2O and Na_2O (and for that matter the other alkalis and alkaline earths as well) show an increased stabilization by their incorporation in silicates, in particular feldspars and feldspathoids. Only in exceptional cases (absence of Al) will the chalcophile tendency of potassium become important; in some rare enstatite chondrites the mineral djerfisherite ($K_3Cu(Fe, Ni)_{12}S_{14}$) has been discovered. The increased stabilization has been quantitatively indicated by the length of the horizontal arrows in the case of K and Na (as well as for Ca and W), and has been qualitatively indicated in the case of Li, Ba, Sr, Rb and Cs. A similar situation arises with minor elements like Cu and As, which will show an enhanced chalcophile character because they

[1]Manuscript received: 1979–08–23.
Revised manuscript received and accepted: 1979-12-11.
[2]Dept. of Geochemistry, State University of Utrecht, UTRECHT, The Netherlands.

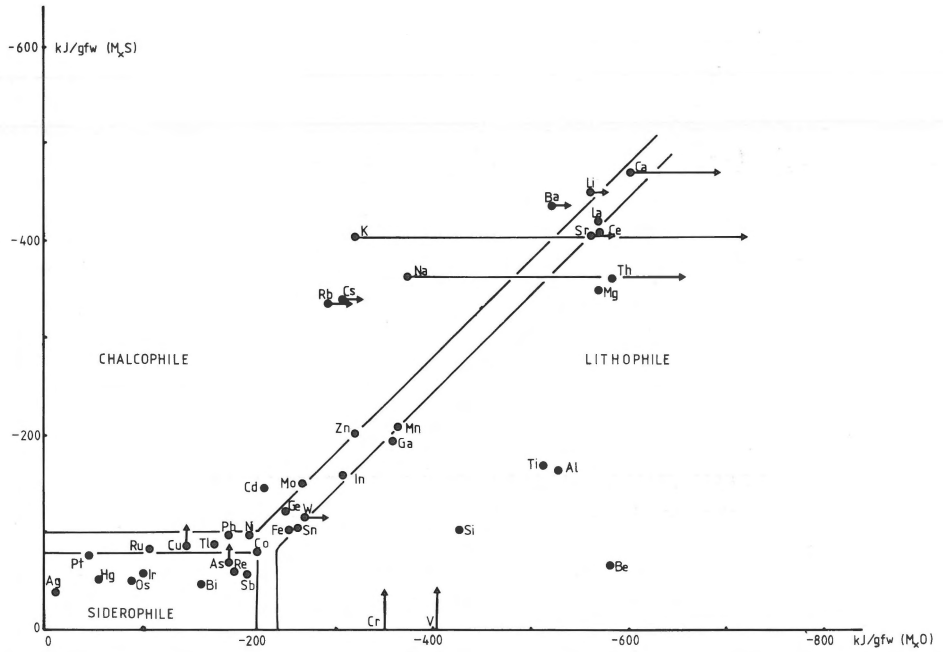

Fig. 1
Gibbs energies of formation of oxides and sulphides at 298 K and 1 Bar, normalized to 1 O and 1 S in kilo Joules/gram formula weight (kJ/gfw). Arrows indicate the direction in which an oxide or sulphide will usually become stabilized by its incorporation in more complex molecules. For K, Na, Ca and W the length of the arrows indicates quantitatively the stabilization of the oxides in leucite, nepheline, wollastonite and scheelite respectively.

combine with the major element Fe in minerals like chalcopyrite ($CuFeS_2$) and arsenopyrite (FeAsS).

Figure 1 has been constructed from thermodynamic data at 1 atm. pressure and room temperature. The general topology of the diagram, and the relative position of the elements do not markedly change with increasing temperature, although the absolute values vary strongly. Most processes which determine the distribution of an element (like condensation from the solar nebula, meteorite formation, differentiation of the earth, endogenic ore and rock formation, metallurgical processes) take place at elevated temperatures. This may be the main reason for the poor separation of the siderophile and the chalcophile field. If we consider the siderophile elements Pt, Ir, Ru, Os, Re, Co and Ni and the chalcophile elements Ag, Hg, Bi, As, Tl, Pb, Sb, which all plot in the 'siderophile field' or in the transition zone between siderophile and chalcophile, their main difference is their melting point. Whereas all the siderophile elements have melting points above 1450 °C, all the chalcophile elements enumerated above have melting points below 1000 °C; Cu, which in effect has an intermediate character, has a melting point of 1083 °C. A similar situation holds for the boiling points of these two groups of elements, copper again occupying an intermediate position. It seems likely that the average temperature at which the elements expressed their geochemical character in major differentiation processes was lower in the case of the chalcophile elements mentioned above, than in the case of the siderophile elements.

For a number of elements, like V and Cr, no data are available for the Gibbs energies of formation of their sulphides. Knowing that they are lithophile in character, we can conclude that the Gibbs energy of the sulphides of Cr and V normalized to 1 S must be larger than (less negative than) -170 and -220 kJ/mole resp.

In conclusion it must be said again, that the statement that an element is chalcophile or lithophile is only useful when considered in its geochemical context.

ACKNOWLEDGEMENT

I wish to thank Dr. H. A. J. Oonk for his probing remarks.

REFERENCES

Garrels, R. M. & C. L. Christ 1965 Solution, minerals and equilibria – Harper & Row (New York).

Kubaschewski, O. & E. LL. Evans 1958 Metallurgical thermochemistry – Pergamon Press (Oxford).

Murthy, V. R. & H. T. Hall 1970 The chemical composition of the earth's core: possibility of sulfur in the core – Phys. Earth Planet. Interiors 2: 276-282.

Rankama, K. & Th. G. Sahama 1950 Geochemistry – Univ. Chicago Press (Chicago).

Robie, R. A., B. S. Hemingway & J. R. Fisher 1978 Thermodynamic properties of minerals and related substances – Geol. Surv. Bull. 1452 (Washington).