TITLE: THE GEOCHEMICAL CLASSIFICATION OF FRACTIONALLY CHARGED ELEMENTS

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THE GEOCHEMICAL CLASSIFICATION OF FRACTIONALLY
CHARGED ELEMENTS*

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SUMMARY

The fundamental unit of electric charge is now known to be $1/3e$. It is therefore natural to ask if elements with fractional charge exist in trace amounts as an intrinsic part of matter. An experimental group at Stanford University has concluded that they do. An effective search for fractionally charged elements in the Earth requires an understanding of their geochemistry. Laws governing the geochemical distribution of ordinary elements are postulated and extended to fractionally charged elements which are classified as lithophile, siderophile, or chalcophile. Previous geochemical distribution laws based on the ionization potentials or electronegativity of an element do not correctly identify the basic factors responsible for geochemical differentiation and therefore do not correctly predict the geochemical behavior of fractionally charged elements. The net

charge of fractionally charged elements decreases their volatility so that they may be concentrated in meteoritic samples of early solar system condensates.

INTRODUCTION

The quantization of electric charge was first suggested by Faraday's experiments on the electroplating of metals and finally confirmed nearly a century later by Fletcher and Millikan (1, 2). Until 1964 the quantum of charge was believed to be the charge, e, of the electron; the quantum is now known to be $e/3$ (3, 4). Quarks, the constituents of protons and neutrons have charge $2/3e$ or $-1/3e$. It is therefore natural to ask if isolated particles of fractional charge $\pm 1/3e$, $\pm 2/3e$, $\pm 4/3e$,... exist freely as elements of the Earth. William Fairbank's group at Stanford University has unequivocally concluded that they do (5, 6). There are now a number of experiments, using a variety of techniques, that will check Fairbank's finding (7-10). They will also extend the search for fractionally charged particles to a wide variety of materials.

Fractionally charged particles are of possible economic interest because of their potential for the catalysis of exothermal nuclear reactions (11). They may also serve as useful indicators of geochemical and cosmochemical fractionation histories of rocks.

Detection of fractionally charged particles. In one experiment (7), a stream of uniformly sized drops is generated in a vacuum and passed vertically downward through a transverse constant electric field. The charge on the drops is determined by measuring the deflection of the drops. The charge on the drops is expected to be measured with an accuracy of $0.02e$. Since the droplets all have the same mass, they are separated into streams according to their quantized charge. Drops with different charges are therefore spatially separated at the ends of their trajectories, and any

drops containing fractional charges may then be collected and recirculated through the system. Therefore, the detector of fractional charge may also be its concentrator.

Virtually any substance can be either dissolved or suspended in the drops. A universal assay for fractionally charged particles will therefore be available. Preliminary estimates indicate that this technique will be able to detect fractionally charged particles at concentrations of one in 10^{23} atoms.

Stability of fractionally charged particles. The existence of a fractionally charged particle in a free state implies that at least one kind of fractionally charged particle is stable, since charge is conserved in particle reactions. Conservation of charge requires that a fractionally charged particle either be stable or decay into one or more other fractionally charged particles, each lighter than the first. Any given fractionally charged particle therefore leads to at least one sequence of fractionally charged particles, decreasing in mass, the sequence terminating at a stable fractionally charged particle.

Where do fractionally charged particles come from? The "big bang" provides a potential source of fractionally charged particles. These fractionally charged particles interacted with nucleons and the helium and lithium nuclei present in the early universe, possibly forming complex systems of relatively small fractional charge. Subsequently, a substantial fraction of matter entered stars, enabling fractionally charged particles to interact with heavier nuclei.

Fractionally charged particles might be found in isolation or in association with particular nuclei. It is currently not possible to predict which nuclei these might be. The search for fractionally charged particles must therefore be extensive, covering many possible cases.

Fractionally charged elements. Negative fractionally charged particles will be bound to ordinary positively charged nuclei by electrical forces, yielding positive fractionally charged nuclei (12). These nuclei will surround themselves with

electrons, much like ordinary nuclei, forming fractionally charged elements.

Positive fractionally charged particles may or may not be attracted to ordinary nuclei. In either case a fractionally charged element will be formed. A negative or positive fractionally charged particle will therefore form a fractionally charged atom consisting of a relatively small positive fractionally charged center surrounded by an electron cloud of ordinary atomic dimensions. The interactions of a fractionally charged atom with ordinary atoms are therefore governed by the familiar laws of chemistry.

Geochemical behavior. In order to mount an effective search for the fractionally charged elements it is necessary to understand the laws of chemistry that will control their fractionation among the major cosmochemical reservoirs and, on a finer scale, the various minerals and rocks that comprise these reservoirs. We propose that the two most fundamental characteristics of an element that determine its geochemical fractionation are first, its volatility, and second, the type of chemical bonds it forms. The former will control chemical fractionation during gas-solid and gas-liquid reactions, and the latter chemical fractionation during condensed-phase reactions. This paper therefore begins with a review of how these factors control the distribution of ordinary elements among the major cosmochemical reservoirs. These factors are then used to predict the basic-geochemical behavior of fractionally charged elements. The factors affecting distribution of fractionally charged elements among various minerals and rocks within these reservoirs (i.e., during solid-liquid and solid-solid reactions) will be treated in a later paper.

GEOCHEMICAL CLASSIFICATION OF ORDINARY ELEMENTS

Condensation. The formation of the Earth from the condensing gas of the early solar nebula is thought to have proceeded by two major steps involving different types of chemical fractionation. The first involved condensation of solid particles from the gas phase. Chemical fractionation in this step was presumably controlled by gas-solid equilibria between minerals and various gaseous species. Many of the potential gas-solid reactions have been described by Grossman (13) and Grossman and Larimer (14), and the various elements may be ranked according to their volatility (14). The more volatile elements are observed to be depleted in the Earth's crust relative to estimates of their solar abundance.

Condensed-phase fractionation. The second step involved separation of immiscible liquids in the accreting planetary bodies. Chemical fractionation in this second step was controlled by liquid-liquid equilibria which were strongly influenced by the activities of oxygen and sulfur. This stage of fractionation gives rise to a geochemical classification in which elements are grouped into three categories; lithophile, sidero-phile, and chalcophile. These categories, plus a fourth category, atmophile, corresponding to the most volatile elements, were proposed by Goldschmidt (15, 16) in analogy with the behavior of elements in smelter furnaces in which three liquid phases; a silicate-oxide, a metal, and a sulfide, plus a gas, coexist. Iron, the most abundant metal, enters all three liquid phases and thereby controls the activities of oxygen and sulfur. The other elements then partition among the four phases. These reducing conditions are thought to have controlled element partitioning among the various classes of fractionated meteorites and between the core and mantle of the Earth.

Reducing conditions. The classification into the three condensed-phase categories might be best defined on the basis of measurements of experimental liquid-liquid fractionation in which three phases are present with fixed activities of

oxygen and sulfur. However, there have been too few experiments to assign categories to all elements. The classification most used is based on the measured abundance of elements in the various types of meteorites which are presumed to be the products of liquid segregation, and on measured abundances of minor elements in meteoritic sulfides. A useful compilation of meteorite analytical data has been edited by Mason (17). These data are observed to be generally consistent with trace element distribution measurements between experimentally produced liquid phases (18). Further, the classification generally reflects the type of minerals an element will enter under given oxygen and sulfur activities independent of the type of fractionation involved. Thus, the classification also reflects the element distribution among phases with no history of liquid fractionation (e.g. refractory inclusions in the Allende meteorite). The classification categories illustrated in Fig. 1 are those of Goldschmidt (19) with minor modification based on Mason's compilation. A few elements such as C, P, Fe, Ga, Ge, and Sn do not exhibit strong partitioning into only one phase, and so are shown in more than one category.

Terrestrial conditions. In the crust and mantle of the Earth, iron metal is not present; oxygen and sulfur activities are here constrained by $FeO-Fe_2O_3$ and $FeS-FeS_2$ equilibria. Under such conditions of higher oxygen and sulfur activities, several elements change their behavior; in particular, C and P become lithophile, and Ni, Co, Mo, and Re become chalcophile. The classification categories under this more oxidizing (and sulfidizing) regime are illustrated in Fig. 2. This second regime was termed "terrestrial" by Goldschmidt (19), and this terminology will be adopted here. Classification in this regime is based on the mineralogy of occurrences of each of the elements in common igneous and hydrothermal rocks of the Earth's crust. Other environments may also be defined which reflect the mineralogy of elements under extreme environments of oxygen and sulfur activity (e.g. atmospheric oxygen).

Objective. The objective of the current work is to determine the geochemical

behavior of fractionally charged elements in the accretion and differentiation processes of the Earth. To do this, we assess the volatility of fractionally charged elements, determine the chemical basis for the geochemical categories of ordinary elements, and then assign fractionally charged elements to these geochemical categories in the various regimes defined by oxygen and sulfur activity.

The chemical basis for geochemical categories. The early classification system proposed by Goldschmidt is empirical. There exists no satisfactory chemical definition based on measurable properties of the elements which would permit straightforward classification. For reducing environments, the classification is based largely on chemical analyses of different classes of, and phases in, meteorites. This classification is generally consistent with measurements of partition coefficients between liquids of various compositions under reducing conditions of oxygen and sulfur activity.

There have been several subsequent attempts to define the categories in terms of measurable chemical properties. Rankama and Sahama (20) classified as lithophile those elements that have heats of formation of the oxide greater than that of FeO. Ahrens (21) suggested that the ionization potential might be a useful indicator of geochemical classification. Ringwood (22) suggested that the Pauling electronegativity might be an even better indicator. Ahrens (23) later pointed out that the empirical classification scheme closely reflects the character of bonding in the principal ore minerals of each element or in meteorite minerals containing major amounts of each element. He suggested that the polarizability as measured by the nth ionization potential might be a useful measure of an element's ability to form bonds with sulfur (n is the element's valence). Brownlow (24) briefly mentions correlation of electron shell structure with geochemical classification, but does not elaborate on how these relate to bond type.

Inadequacy of ionization potentials and electronegativity. For an ordinary ele-

ment, ionization potentials and electronegativity are very strongly correlated with each other and with the electron shell structure and the type of bonds the element may form. It is therefore difficult to decide which factors are fundamental in determining geochemical behavior. Consideration of fractionally charged elements allows some critical distinctions to be drawn. Addition of a fractional charge to a nucleus substantially alters its ionization potentials and electronegativity while having little effect on its electron shell structure and hence on the type of bonds it forms. For example, consider the very common ionic substitution of aluminum for silicon in tetrahedrally coordinated sites in framework silicates. If Al^{+3} may substitute for Si^{+4} in substantial proportions, then any atom with a nucleus of fractional charge lying between the nuclear charges of aluminum and silicon will also substitute in that site. This substitution should occur despite the fact that the fractionally charged atom has substantially different electronegativity and ionization potentials from either aluminum or silicon (12). The fractionally charged atom is expected to display bond type similar to those of its neighboring ordinary elements in the same row of the periodic table, since bond type is determined primarily by the electron shell structure and not by electronegativity or ionization potential.

Bonding. A small change in nuclear charge usually does not significantly alter the type of bonds an elements forms in condensed phases. It can be readily shown that a change of $\pm e/3$ or $\pm 2e/3$ in the charge of a nucleus has little effect on the energy released in the formation of its ionic bonds, because the change in energy required to remove its valence electrons is approximately canceled by the change in electrostatic energy of the ion in an ionic crystal. This approximate cancellation is responsible for the existence of isoelectronic sequences of crystals such as KF, CaO, ScN, and TiC, where the nominal charge varies by $4e$. Similarly, the existence of isoelectronic sequences of covalent crystals (e.g. CuBr, ZnSe, GaAs, and Ge) indicates that covalent bonding is also not a strong function of nuclear charge, so that the addi-

tion of $\pm e/3$ or $\pm 2e/3$ to the nucleus of a covalently bonding element can lead to a fractionally charged element that also bonds covalently.

We view the volatility of the molecular species of an element and the types of bonds an element may form under various conditions of oxygen and sulfur activity to be the two most fundamental characteristics that determine its cosmochemical fractionation. Consideration of bonding also makes it possible to understand why a given element almost always occurs in a given type of mineral regardless of its fractionation history.

The empirical evidence linking bond type with geochemical categories will now be presented. Bond type may be inferred from electron shell structure under given conditions of oxygen and sulfur activity. Because bond type is, in general, constant over ranges of nuclear charge of several e, assignment of bond type, and hence geochemical category, is possible for most fractionally charged elements. The geochemical classification of the elements under reducing and terrestrial conditions is summarized in Figs. 1 and 2.

Atmophile Elements

The atmophile elements include the noble gases plus H, C, and N. These elements form electrically neutral free atoms or covalently bonded neutral molecules of high vapor pressure (H_2, CH_4, N_2, NH_3). Solids of these atoms and molecules are bonded by relatively weak Van der Waals forces, resulting in their high vapor pressures. These elements would condense very late in the cooling solar nebula gas (14). The Earth is generally thought to have accreted from meteoritic material before cooling had progressed sufficiently for these elements to have condensed. These elements are depleted in the Earth's crust by up to ten orders of magnitude relative to Si-normalized solar abundances (25).

Lithophile Elements

Reducing conditions. The lithophile elements include the halogens, the alkalis and alkaline earths, the first three columns of the transition series, the lanthanides, the actinides, and the elements B, O, Al, Si, Cr, Mn, Fe and W.

Terrestrial conditions. Under conditions of terrestrial higher oxygen and sulfur activity C and P are also lithophile. Under all conditions, oxygen is the dominant anion, and these elements are usually found in oxide minerals, predominantly silicates. Hydroxyl and fluorine are also common anionic species but occur predominantly in lower-temperature, particularly metamorphic, minerals. These elements are strongly partitioned into ionic silicate melts relative to metallic iron and covalent sulfide melts. With the exceptions of Fe, Mn, and W, terrestrial magmatic sulfide minerals of these elements are unknown. Also, with the exception of Fe and C, none are known as native elements.

Ionic bonding. The lithphile elements form dominantly ionic bonds in condensed phases. Electroneutrality with respect to nominal ionic charge appears to be strictly observed in minerals of these elements, and with the exceptions of V, Cr, Mn and Fe, these elements interact with anionic oxygen as ions with filled outer electron shells. Bonding is overwhelmingly ionic so that Pauling's rules (26) are observed fairly closely in minerals of these elements. X-ray diffraction measurements of electron distributions (27) indicate that minerals formed from lithophile elements are indeed composed of ions, although the net charge on the ions is difficult to determine. With the exceptions of V, Cr,-Mn, Fe (28) and, to a lesser extent, Si (27, 29) the ions exhibit strong spherical symmetry. The interatomic distances correspond to the sums of fairly well-defined ionic radii (30-32). Such radii are distinct from those that these elements exhibit in covalent and metallic compounds (26, 33-35). In addition the cohesive energy of minerals containing lithophile elements are close to what would be expected for ionic compounds (26,34).

Substitution. Further evidence for the ionic nature of minerals of the lithophile

elements is given in the rules for the substitution of one element for another. Hetero-valent cation substitutions are generally accommodated by coupled cation substitutions so that approximate electroneutrality is maintained. The lithophile elements enter ionic oxygen liquids (silicate magmas) and partition among the solid phases on crystallization according to regular rules of liquid-crystal fractionation based on ionic radius and charge (36, 37), even when they occur in trace amounts.

Cosmochemistry. The majority of the lithophile elements will have condensed from a gas of solar composition before metallic iron or the sulfides (14). The minerals they form are of much lower density (S.G. = 2.5 - 4.0) than metals or sulfides. Therefore, gravitational segregation eventually concentrated minerals of the lithophile elements in the outer portions of the terrestrial planets. These elements are enriched in the crust and mantle of the Earth relative to solar abundances.

Siderophile Elements

Reducing conditions. The siderophile elements occur in the center of the periodic table. This category is composed principally of the Group VIIIA elements (Fe. Co. Ni, Ru, Rh, Pd, Os, Ir, and Pt). In addition the category includes Mo, Re, and Au. Under reducing conditions, C, P, Ga, Ge, and Sn all exhibit partial siderophile behavior.

Gallium, germanium and tin exhibit somewhat anomalous geochemical behavior in that it differs from the behavior of their dominantly chalcophile neighbors. Although they are enriched in metallic meteorites, they may also occur in minor amounts in meteoritic sulfides and even silicates. These elements are assigned to both siderophile and chalcophile categories under reducing conditions in Fig. 1.

Terrestrial conditions. Under conditions of terrestrial higher oxygen and sulfur activity, all of these elements with the exception of carbon, phosphorus, and gold will form sulfides, and with the exceptions of C, P, Fe, Sn, and Au, the principal ore

minerals of these elements are sulfides.

Metallic bonding. The siderophile elements form dominantly metallic bonds in condensed phases. None of these elements can achieve noble gas configuration except by loss of six or more electrons. These elements do not form ionic or covalent minerals with one another, and the ionic bond strengths of these elements are weak relative to the lithophile elements. Internuclear distances correspond to the sums of the elements' metallic radii (26) which are distinct from their radii in ionic or covalent compounds. The metallic nature of the bonding is also evident from the high electrical conductivities of these minerals.

Carbon and phosphorus are assigned partial siderophile character because they are slightly enriched iron meteorites relative to chondrites. On cooling, carbon and phosphorus enter metallically bonded phosphides and carbides that are much more restricted in stoichiometry than alloys of the other siderophiles. Such minerals as schreibersite (Fe_3P), however, do not exhibit ionic stoichiometries. In contrast to the other siderophiles, carbon and phosphorus are predominantly lithophile under terrestrial conditions, forming closed-shell ions.

Substitution. The transition elements of this group have similar metallic radii, they substitute for one another readily, and typically alloys in all proportions may occur.

Cosmochemistry. The platinum-group metals are extremely refractory and are among the first elements to condense (14). Iron and the other siderophiles condense after most of the lithophiles, but before the chalcophiles. The siderophile elements are all enriched in the iron meteorites relative to chondrites. These elements are strongly depleted in silicate and oxide phases in meteorites and in the crust and mantle of the Earth. Depletion in the crust and mantle is thought to result from chemical fractionation of these elements into a metallic phase and subsequent gravitational segregation of the denser metal into the core.

Chalcophile Elements

Reducing conditions. The chalcophile elements occur on the right side of the periodic table. This category consists primarily of sulfur plus the group "B" elements (38) of rows 4, 5, and 6 of the periodic table other than the halogens.

Terrestrial conditions. Under terrestrial conditions of oxygen and sulfur activity, the chalcophile category will also include all of the elements that are siderophile under reducing conditions except phosphorus and carbon.

Covalent bonding. The chalcophile elements form dominantly covalent bonds in condensed phases. None of these elements can achieve a noble-gas electron configuration except by addition of more than one, or loss of more than six, electrons. These elements do not form ionic minerals with one another, and their ionic bond strengths are weak relative to the lithophiles. The s, p, and possibly d orbitals hybridize around these elements, and these orbitals overlap one another to form crystals. The hybrid bonding orbitals in these minerals typically accept electrons from sulfur (or As, Se, or Te) (26,35,39,40). Such bonding exhibits strong directionality, and internuclear distances are not equal to sums of ionic or metallic radii, but rather to sums of covalent radii (26, 33).

Substitutions. Substitutions by elements in the same column of the periodic table are common, whereas heterovalent substitutions, such as those by atoms adjacent in the periodic table, are relatively rare in these minerals. Where they do occur, they typically involve coupled substitution, such that the total number of electrons and bonding orbitals remains constant. For example, GaAs and ZnSe form a complete solid solution series which has the sphalerite structure. This series of compounds may be considered isoelectronic, although not ionic. The substitution of atoms differing in nuclear charge by 1e will not greatly affect the structure as long as the total number of electrons and available orbitals remains constant. In such structures, vacancies are common, and stoichiometries are, in general, more complex

than in oxides (41).

Of particular significance in understanding the chemical behavior of the chalco-phile elements is the observation that substitution of noble-gas-ion elements (i.e. lithophiles) is virtually unknown in these minerals. The rules of element substitution are clearly quite different from those in ionic compounds. Not only radius, but also orbital geometries must match before substitution can occur. Thus, chemical substi-tutions are much more limited than in ionic compounds.

Cosmochemistry. These elements are depleted in the Earth's crust relative to their solar abundances, although less depleted than the siderophiles. This depletion may stem from either or both of two different chemical effects. First, the increased volatility causes them to condense later than most of the lithophiles and siderophiles (14). The Earth may then have accreted from meteoritic material before condensa-tion of most of these elements. Second, if a sulfide liquid were present in the early Earth as suggested by Goldschmidt (19), these elements would be strongly frac-tionated into this sulfide phase which would sink below the crust and mantle.

Although chalcophiles are usually found only in trace amounts in ionic silicate melts, these systems may dominate their geochemical behavior in the crust of the Earth. In these systems, chalcophiles may become concentrated in residual liquids to form accessory magmatic sulfide minerals or enter late-stage, volatile-rich fluids to be deposited as hydrothermal sulfides. However, the exact nature of their behavior in ionic melts and minerals is not well understood.

Summary

From the foregoing discussion of shell structure, bonding, and element distribu-tions in nature, several principles emerge which suggest working rules for the geo-chemical classification of ordinary elements. There are primarily three types of bonds in natural condensed phases. The type of bonds an element forms are

expected to be the same in liquids and solids. Each bond type is associated with a geochemical category. Oxygen and sulfur activities may affect the type of bonds an element forms, and hence its geochemical classification. Determination of bond type for an ordinary element therefore leads to a prediction of relative enrichment or depletion of that element in the various cosmochemical reservoirs and to a prediction of the types of minerals in which it is likely to be enriched. The bond type may usually be inferred from the electron configuration of the unbonded atom and the abundances (activities) of oxygen and sulfur. Because isoelectronic substitution can occur over substantial ranges of atomic number in lithophile (ionic), siderophile (metallic), and chalcophile (covalent) minerals, it appears that the loss or gain of 1e in charge on the nucleus of an element usually has only minor effect on its bonding in condensed phases, unless it lies near boundaries between geochemical categories in the periodic table.

Rules. We therefore suggest the following rules for the geochemical classification of ordinary elements based on bonding in minerals. The bonding is controlled by electron shell structure and oxygen and sulfur activity. The first four rules apply to reducing conditions and governed chemical fractionation during the accretion and early differentiation of the Earth. The resulting classification is shown in Fig. 1. The last rule applies to terrestrial conditions and governs chemical fractionation in the crust and mantle (Fig. 2).

[1] Elements that form solids bonded by weak Van der Waals forces will be atmophile. This category includes the noble gases with their filled outer electron shells and certain elements that combine with hydrogen to form simple neutral molecules of high vapor pressure (Group VIIIB plus C, N, and H).

[2] Elements that form dominantly ionic minerals will be lithophile. This category primarily consists of elements whose ions have a filled outer s and p electron shells, but also includes the transition elements, V, Cr, Mn, and Fe.

[3] Elements that form dominantly metallic minerals will be siderophile. This category includes elements with partially filled d-shells that cannot achieve noble gas configuration except by loss of six or more electrons (Group VIIIA plus Re, Mo, and Au). Phosphorus, gallium, and the Group IVB elements, C, Ge, and Sn, exhibit partial siderophile behavior.

[4] Elements that form dominantly covalent minerals will be chalcophile. This category includes those elements that have hybrid *sp* orbitals available, outside of a filled 18-electron (*s*, *p*, and *d*) shell, for acceptance of electrons from S, Se, As, or Te. (Groups IB through VIB of rows 4, 5, and 6. Gold, however, forms covalent bonds only with tellurium, and so is usually not included in this group.)

[5] Under conditions of higher (terrestrial) oxygen and sulfur activity typical of the Earth's crust and mantle, all of the elements classified as siderophile under reducing conditions except those lacking d-electrons will form complex hybrid covalent bonds with S, As, Se, and Te, and be chalcophile. Those lacking d-electrons may achieve noble-gas configuration and be lithophile. Gold and the platinum-group metals may be siderophile or chalcophile.

Despite their somewhat qualitative nature, these rules offer several advantages over previously suggested guidelines for the geochemical classification of ordinary elements. First, they reflect the cosmochemical fractionation and the mineralogy of ordinary elements more accurately than methods based on ionization potentials, electronegativity, or heats of formation. Second, they are simpler, being based only on bonding in minerals. Third, they may be used to predict the geochemical behavior of most fractionally charged elements.

The association of bond type and geochemical category appears to be a fundamental relationship governing geochemical behavior. As is apparent from consideration of fractionally charged elements, bond type is much more closely related to electron configuration and activities of oxygen and sulfur than to ionization potentials or

electronegativity. Modification of the nuclear charge of an element by $\pm 1/3e$ drastically alters its ionization potentials and electronegativity but leaves the type of bonds it forms in condensed phases, and hence its geochemical classification, largely unaltered.

GEOCHEMICAL CLASSIFICATION OF FRACTIONALLY CHARGED ELEMENTS

Condensation. The assessment of volatility is the first step in understanding the cosmochemistry of fractionally charged elements. The addition of a fractionally charged particle to the nucleus of an atom means that the atom can never be electrically neutral. Further, because abundances must be very low, naturally occurring molecular species containing such an atom will not be neutral. The net electrical attraction, then, of this fractionally charged atom or molecule for an oppositely charged ion, solid particle or liquid droplet should reduce the volatility of the fractionally charged atom relative to integrally charged atoms of similar electron shell structure. This will cause the fractionally charged element to condense earlier in the cooling solar nebula than its integrally charged counterparts. However, the significance of the effect will depend on the net ionization state of the gas. If the gas is highly ionized the effect will be inconsequential. If the gas is not strongly ionized, as estimated by Arrhenius and Alfven (43), and if the cooling rate is slow, the decreased volatility will result in substantial enrichment of fractionally charged particles into the early condensates. Consequences of this enrichment will be explored in the discussion section.

Condensed-phase fractionation. The geochemical classification of fractionally charged elements is determined by the type of chemical bonds they form in condensed phases. This bonding is largely determined by electron shell structure. The type of bonds a fractionally charged element will form may be predicted if its two neighbors in the same row of the periodic table form the same type of bonds. Then the fractionally charged element will behave as its neighbors. For example, the

substitution of aluminum for silicon in tetrahedral sites of the framework silicates was already noted. Both aluminum and silicon have similar electron shell structures and bond primarily ionically in these sites. Therefore, the fractionally charged elements with nuclear charge lying between those of aluminum and silicon ($13^1/_3$ and $13^2/_3$) are expected to bond similarly at these sites. The geochemical behavior of the fractionally charged elements will be outlined below. The geochemical classification of the fractionally charged elements under reducing and terrestrial conditions is summarized in Fig. 1 and 2.

Atmophile Fractionally Charged Elements

Because fractionally charged atoms cannot be electrically neutral they should exhibit lower volatilities than integrally charged atoms with similar electron shell structure. Therefore, no fractionally charged element is expected to be atmophile. The atmophile elements are depleted in the Earth's crust by ten orders of magnitude or higher for He (25) relative to solar-system abundances. Fractional variants (42) of the noble gases are expected to form primarily ionic bonds and therefore exhibit lithophile behavior.

Lithophile Fractionally Charged Elements

Fractionally charged elements that form dominantly ionic bonds will be lithophile. The fractionally charged elements that will most certainly form ionic bonds are those whose two neighbors in the same row of the periodic table exist in nature as ions with the same filled outer electron shell. This group will include fractional variants of the noble gases. Elements with fractional nuclear charges lying between He and B ($2^1/_3$ to $4^2/_3$) should behave as ions with a filled He shell (2 electrons). Similarly, atoms with fractional nuclear charge between O and Si ($8^1/_3$ to $13^2/_3$), Cl and Ti ($17^1/_3$ to $21^1/_3$), Br and Nb ($35^1/_3$ to $40^2/_3$), I and La ($53^1/_3$ to $56^2/_3$),etc. should also behave as noble-gas ions. Under oxidizing conditions, each of these noble-gas-ion

series may extend to higher nuclear charge. Elements of fractional nuclear charge with partially filled $4f$ or $5f$ electron shells inside a filled s and p shell (i.e. the lanthanides and actinides) will also be lithophile. Elements of fractional nuclear charge which have partially filled d shells and which lie between lithophile ordinary elements (i.e. V, Cr, Mn, and Fe) should also form dominantly ionic bonds.

Siderophile Fractionally Charged Elements

Fractionally charged elements that form dominantly metallic bonds will be siderophile. Fractionally charged elements between Fe and Ni ($Z = 26^1/_3$ to $27^2/_3$), Ru and Pd ($Z = 44^1/_3$ to $45^2/_3$), and Os and Au ($Z = 76^1/_3$ to $78^2/_3$) will most likely bond metallically because the integrally charged elements in these ranges of nuclear charge all substitute for one another in metallic minerals. The fractionally charged variants of these elements are expected to be depleted in the Earth's crust by several orders of magnitude relative to their abundances in the primitive solar nebula.

Chalcophile Fractionally Charged Elements

Fractionally charged elements that form dominantly covalent bonds will be chalcophile. Under reducing conditions these will be elements that have sp hybrid orbitals available outside a filled 18-electron shell. This group will include fractionally charged elements between Cu and Se ($29^1/_3$ to $33^2/_3$), Ag and Te ($47^1/_3$ to $51^2/_3$), and Hg and Po ($80^1/_3$ to $83^2/_3$). Under terrestrial conditions, this group will extend further to the left in the periodic table where covalent bonds will include hybridized d-orbitals.

Fractionally Charged Elements of Uncertain Classification

If the geochemical behavior of a fractionally charged element's two ordinary neighbors in the same row of the periodic table differ, then the behavior of the fractionally charged element is difficult to predict. Fractionally charged elements that have not been assigned to a geochemical category are designated by unshaded areas

in Fig. 1 and 2.

DISCUSSION

Platinum-group metals are among the earliest elements to condense from the cooling solar nebula gas, followed by refractory calcium and aluminum oxide minerals (14). These phases have been identified in the calcium and aluminum-rich inclusions (CAI) in the Allende meteorite (44). The addition of a fractional charge to the nucleus of an atom lowers its volatility. This results from the attraction of the net fractional electric charge of the atom for its image charge on the metal particles or for oppositely charged surface ions on the oxide particles. As mentioned earlier, the significance of this effect will depend on several factors, among them, the net ionization state and the cooling rate of the gas. If the effect is important, the siderophile fractionally charged elements will be enriched in noble metal particles, and the lithophile fractionally charged elements enriched in the oxide phases associated with the calcium and aluminum-rich inclusions in the Allende meteorite.

Once incorporated in the Earth, fractionally charged elements will fractionate according to their geochemical classification in a manner similar to ordinary elements. Just as with ordinary elements, a large atomic weight does not necessarily imply segregation into the core. Unless they are extremely heavy, lithophile fractionally charged elements will be buoyed up by associated oxygens and be enriched in the crust and mantle. Incompatible lithophiles (45) will tend to remain in silicate liquids and be concentrated in the crust, particularly the continental crust. Such elements are expected to be strongly enriched in pegmatites (46). Similarly, the siderophile fractionally charged elements are expected to be enriched in the metallic core.

The identification of fractionally charged elements as an intrinsic part of matter and the potential for their detection at exceedingly low concentrations raise the possibility that fractionally charged elements may serve as very sensitive indicators of

the chemical fractionation history of the Earth and other geochemical reservoirs. For example, if the separation of a sulfide melt during differentiation of the Earth is responsible for the observed depletion of the chalcophile elements in the Earth's crust, then the fractionally charged chalcophiles should be depleted by similar factors. However, if the chalcophile's volatility is responsible for the observed depletion (47), then the fractionally charged chalcophiles might be less depleted than ordinary elements with the same electron structure. In either case the classification category and the terrestrial chemical behavior of the fractionally charged chalcophile elements should not be affected.

CONCLUSIONS

The relationships among electron shell structure, bonding in minerals, and geochemical classification of ordinary elements have been explored. The geochemical classification of an ordinary element is determined by the type of chemical bonds it forms in condensed phases, rather than by it ionization potentials or electronegativity. This basis for geochemical classification has been extended to fractionally charged elements. The nature of bonding, and therefore the condensed-phase geochemistry, of ordinary elements is not strongly dependent on their nuclear charge. In general, elements adjacent in the same row of the periodic table exhibit rather similar bond type and hence similar geochemical behavior. We predict that elements with fractional nuclear charge will exhibit geochemical behavior similar to their two neighboring ordinary elements. This principle allows geochemical classification of most fractionally charged elements.

Despite similarities in condensed-phase chemistry, it appears that large differences in geochemical behavior may occur between fractionally and integrally charged elements when a gas phase is involved in a chemical reaction. Because fractionally charged atoms can never be neutral, they should exhibit lower volatilities than integrally charged atoms of similar ele ron shell structure, particularly if the

net ionization state of the gas is low and the cooling rate is slow. This leads us to predict potentially significant enrichment of fractionally charged elements in early condensates from the solar nebula.

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FIGURE CAPTIONS

Fig. 1. The periodic table of ordinary and fractionally charged elements shaded according to their geochemical classification under reducing conditions. The ordinary and fractionally charged elements are arranged in rows according to increasing nuclear charge. Elements with similar electron shell structure lie in the same column of the periodic table. Each ordinary element together with its fractional variants (42) is shown as a box subdivided in three with the symbol of the ordinary element. The geochemical classification of unshaded fractionally charged elements is uncertain. Ordinary elements with an X do not have sufficiently long-lived isotopes to behave as independent species in geochemical systems.

Fig. 2. The periodic table of ordinary and fractionally charged elements shaded according to geochemical classification under conditions of terrestrial oxygen and sulfur activities.
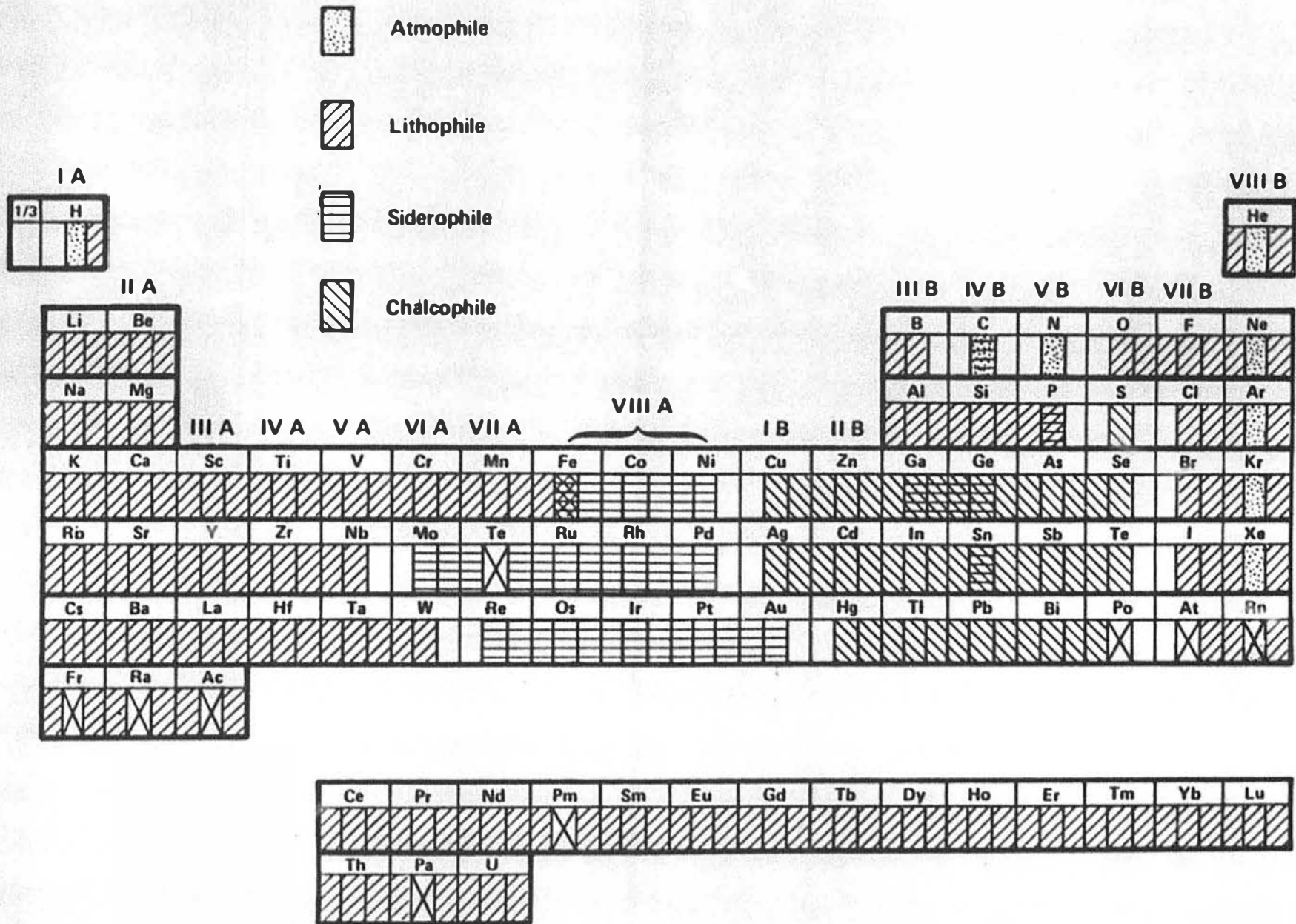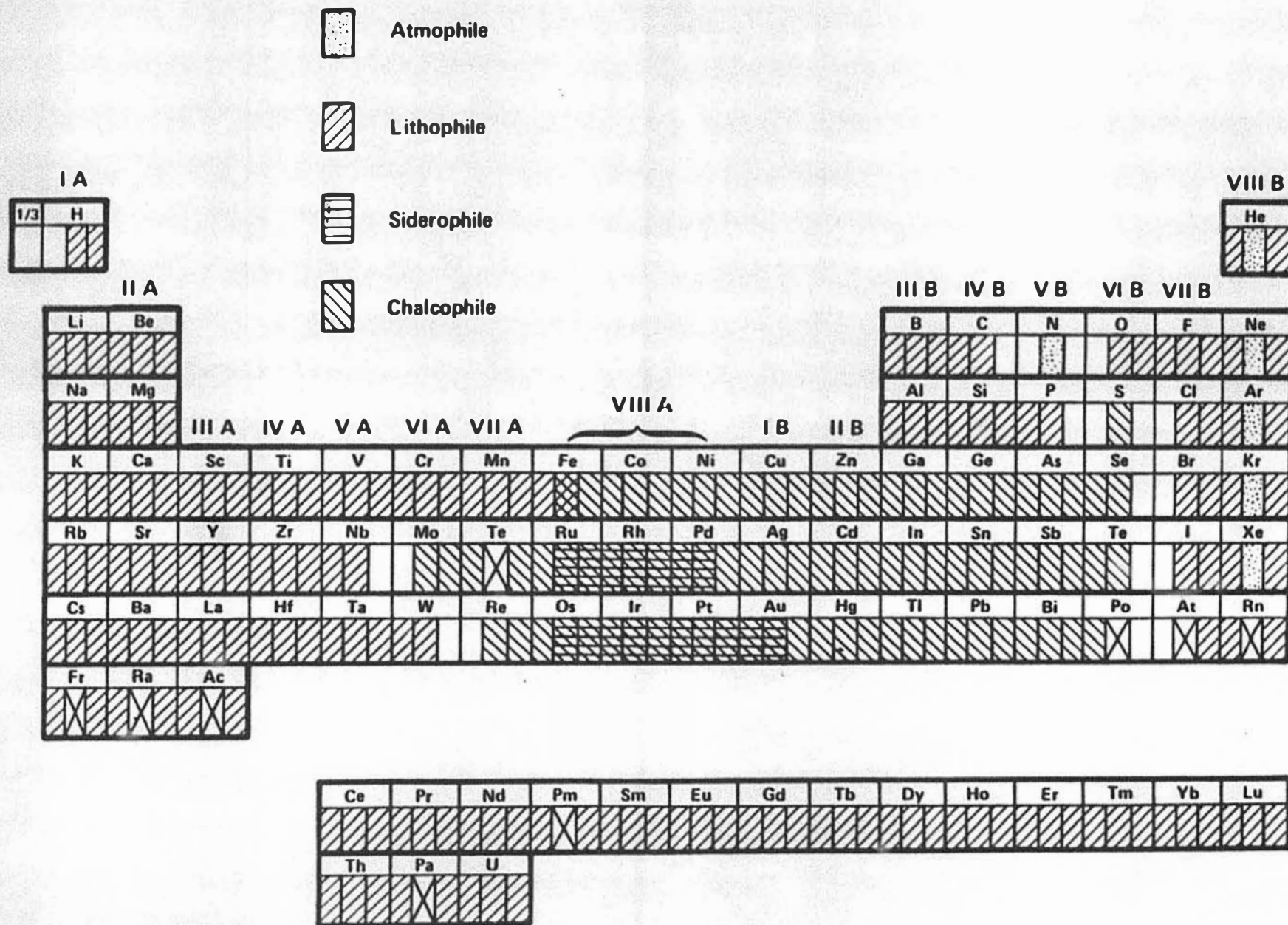
Figure 1

Figure 2