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# ISOMORPHISM AND ENDOCRYPTY: NEW APPROACHES TO STUDY THE BEHAVIOR OF TRACE ELEMENTS IN MINERAL SYSTEMS

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The known notions of limiting concentration of impurities and isomorphous capacity of minerals have been applied to defective crystals, using the concept of endocrypty, reinterpreted as a mode of incorporation of impurity atoms into the real structure of host minerals. It is shown that experimental studies of mineral systems containing trace elements (TE) should be based on analysis of factors facilitating structural incorporation of TE into minerals. Limiting the concentration of TE is correlatable with a maximum density of defects in a crystal which causes the strongest influence on incorporation of the impurity and can be estimated on this basis for different specific conditions; extrapolation to zero defect density shows isomorphic capacity of a mineral with respect to a given TE. In particular cases when a trace element cannot form a separate phase limiting its solubility in the host mineral, special components are recommended to be used which are additional elements or complexes facilitating saturation of the fluid phase and the respective crystallizing mineral by combining them with TE to form intermediate phases. This approach has a difficulty in discriminating modes of occurrence of TE in a saturated phase. This difficulty can be overcome by considering undersaturating TE concentrations in the study mineral when it is in phase equilibrium with a "reference" mineral allowing high solubility of these trace elements. In a general case, besides the curve of the true phase equilibrium corresponding strictly to isomorphism of TE, there are a number of additional apparent phase equilibrium curves depending on the types of crystal defects and their role in endocrypty. Correspondingly, the constant of impurity distribution can deviate from the true isomorphic cases. Thus, in the case of endocrypty, the limiting concentration of incorporated TE is not constant at specific  $P$  and  $T$  values but depends on the conditions under which the real crystal formed and on the character of its defects. It is suggested to apply the earlier proposed concept of forced equilibria to analyze different modes of incorporation of TE attributed to structural defects of minerals.

*Isomorphism, endocrypty, trace elements, limiting concentration of incorporated TE, isomorphous capacity, solid-state geochemistry, experiment*

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## INTRODUCTION

Trace elements (TE) are widely used in geochemical studies as a source of information about the environment and conditions of mineral genesis [1], as indicators for identification of magma mixing, partial melting, mineral fractionation during differentiation, etc. [2]. At the same time, TE are involved in some problems the solution of which is critical for obtaining valuable geochemical information. One of them is an ultimately important problem of whether or not Henry's law is valid in the region of very low concentrations of a component. The opposite opinions exist, and, strangely enough, both of them are confirmed by certain empirical information (analysis of its safety is beyond the scope of this paper). Thus, some researchers believe that the systems do not satisfy Henry's law in the region of low concentrations [3]; others are sure that, to the contrary, deviations from ideal mixtures are typical of the higher concentration region and only there Henry's law does not hold [4]; and the still others suppose all information about the failure of the law for trace

components follows from analytical and experimental errors [5]. These contradictory opinions are, certainly, due to the intricacy of the experimental study of TE behavior. The methodology of this kind of investigation must be essentially different from the conventional experimental and analytical approaches to the study of trace components. The goal of the present paper is to offer a new experimental procedure for studying TE behavior in geochemical systems taking into account modern concepts of solid geochemistry on real crystals and interaction of defects, TE being some kind of them. The main subject of solid geochemistry is to study structurally imperfect (defect) crystals and their host mineral systems as well as the behavior of chemical elements (including trace elements) during the formation and various postcrystallization transformations of real natural crystals [2]. This approach is especially important for TE because their concentration is often commensurate with the concentration of defects in mineral crystals and the energies of interaction with defects are higher than the energies of mixing at regular sites of the ideal structure. This leads to a drastic increase in the coefficient of distribution of an element in the microconcentration region, to the so-called effect of trapping, which may be one of the most important reasons for deviation of TE behavior from Henry's law [6].

### LIMITING CONCENTRATIONS AND FORMS OF OCCURRENCE OF DOPANT AND ISOMORPHOUS CAPACITY OF MINERAL

Figure 1 shows three possible versions of TE behavior in an experiment on saturation of a certain mineral phase. The first case (line 1) is the formation of an isomorphous mixture in its classical sense, when the continuous miscibility exists between the mineral phase and corresponding own "marginal" phase of the trace element. Line 2 corresponds to the so-called "isodimorphism" [7], when the marginal phase of TE is not isostructural to the mineral under study or to the gap miscibility (decomposition) of a solid solution. In this case, the miscibility is limited by the appearance of a new phase, and the miscibility limit corresponds to the plateau on line 2. The third case (see Fig. 1, line 3) is observable when the marginal compound of the trace element is absent (i.e., one of the mixture components is imaginary). The geochemical analog of this case is called endocrypty [8] and describes the situation when the dopant cannot form its own compound but is dissipated in the crystal structure of a compound with similar crystallochemical properties. If the TE concentration in a fluid is increased in the experiment, e.g. owing to certain additional elements or complexes, it is possible to reach the state when the structural component of the TE admixture stops changing (or change only slightly, see Fig. 1) by increasing its content in the coexisting fluid phase. At the same time, the element concentrations due to nonstructural forms of its occurrence may increase. In this case, as noted in [9], the above-mentioned additional elements take part in the construction of TE-coexisting unstable but real intermediate phases playing the role of virtual marginal phases limiting TE solubility in the mineral. However, since the composition of these phases is usually not known exactly and principally may vary with concentration, there may be no distinct plateau indicating saturation on line 3. Nevertheless, if different dopants are used in

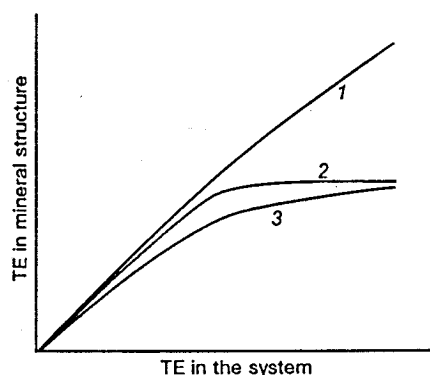


Fig. 1. Possible versions of the behavior of a TE in an experiment on its saturation with an arbitrary mineral phase. 1 — real isomorphism, when the mineral under study and corresponding phase of the trace component form an ideal mixture; 2 — isodimorphism, under which the marginal phase of the trace element is not isostructural to the mineral of interest or gap of miscibility (decomposition) of the solid solution; 3 — there is no marginal compound corresponding to the desired mineral (one of the "mixture" components is imaginary).

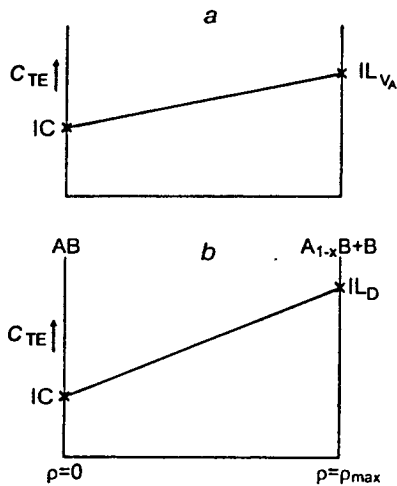


Fig. 2. Possible versions of estimation of the influence of mineral crystal structure defects on limiting concentrations of the incorporated trace element. *a* — Governing defects are vacancies in sublattice A of a nonstoichiometric mineral  $A_{1-x}B$  (e.g., pyrrhotite  $Fe_{1-x}S$ ); *b* — governing defects are dislocations;  $\rho_{max}$  specifies the most possible density of dislocations in a cluster of this kind;  $LC_{V_A}$  is the limiting concentration with participation of vacancies A;  $LC_d$  — the same, with participation of dislocations; IC — isomorphous capacity of the mineral with respect to a given trace element.

a sufficiently wide range of concentrations and the data obtained are extrapolated onto their zero contents, the coinciding results will be certainly indicative of saturation. This approach was used in [9] for estimating the limiting concentration of gold entering the structure of greenockite ( $\alpha$ -CdS) in the presence of additional elements, As or Se. To isolate the structural component of the Au dopant, a combination of autoradiographic and atomic absorption methods was applied.

Despite its apparent simplicity, this approach has several essential restrictions. First, it is necessary to select a set of components that provide the highest TE contents in the fluid (these TE are called hereafter “saturation-favoring components”, SFC\*). But this choice itself is not trivial, especially, when we deal with noble metals (Au, Pt) having weak affinity to the major elements of the hydrothermal medium. Second, to prove saturation, we must use at least two kinds of these components, and to reduce a probability of random coincidence to zero, three kinds are required. But this is not always possible. Third, the separation of TE species aimed at separating just a structurally bound component is hindered in the saturation region. Fourth, we are not sure that the quantity obtained is only the limit of mixing in its classical sense, i.e., in the sense of isomorphous capacity of the ideal mineral structure with respect to a given TE, because under the real experimental conditions we deal with structurally imperfect crystals having defects that are able to interfere with dopant atoms. Therefore, first of all, one must decide which factors critically influence the incorporation of a dopant into a structure.

The last restriction is of a general nature and is pertinent to any method applied to the study of TE incorporation into real crystal structures of minerals. So, we dwell on it. Figures 2, *a*, *b* show possible variations of an experimental solution to the given problem. If the TE incorporation is affected by the own point defects of the AB crystal (e.g., vacancies in the A sublattice), the situation corresponds to Fig. 2, *a*. Varying physicochemical conditions so that they favor generation of metal vacancies in crystals, we can follow a corresponding change in the content of structurally bound dopant to establish the mechanism of its incorporation and limiting concentration. Data extrapolation to the boundary of the region of  $A_{1-x}B$  phase homogeneity from B will give a limiting concentration of TE incorporated into the phase according to a

\* Another term, “conductor elements”, is used in [9], but it is less precise and, moreover, calls an objectionable association with electric current conductors.

mechanism with participation of A vacancies, whereas extrapolation to the AB stoichiometric composition will give an isomorphous capacity of the phase with respect to TE in its classical sense as limiting concentration of a dopant in an ideal crystal. Given that the impurity incorporation into crystal is favored by dislocation defects [10], a similar problem is solved by varying the density of dislocations (see Fig. 2, *b*). In this case we must take into account that various types of dislocation clusters have different abilities to absorb the dopant, i.e., interaction of dislocations with isomorphous dopants depends not only on dislocation density but also on the pattern of its distribution throughout the crystal. For example, the field of stresses of the dislocation wall (symmetrical inclination boundary in crystal) spreads for a distance, approximately equal to the distance between neighboring dislocations in the wall, whereas in the case of a network of edge dislocations, nearly the whole crystal is deformed, because such networks have far-reaching elastic fields [11]. Therefore, the concept of limiting concentration of TE incorporated into a crystal by a dislocation mechanism is somewhat conventional, and the quantity  $\rho_{\max}$  in Fig. 2, *b* should characterize the ultimately possible density of dislocations in a cluster of this kind. The modern methods of electron microscopy permit us to establish both the type of dislocation assembly and the density of dislocations in it, but it is not always possible to vary these quantities in an experiment. Therefore, a chaotic model for dislocation distribution may be accepted in a first approximation. After the relationship of the incorporated impurity with dislocations is established, we can investigate it in more detail, taking into account the real distribution of dislocations in the crystal volume. It is natural that the chaotic model is more appropriate for a region near  $\rho \sim 0$ , until the correlation in mutual disposition of dislocations is minimal. This permits estimation of isomorphous capacity for the case when all other dopant incorporation mechanisms, but dislocational, are not efficient (see Fig. 2, *b*). Note that, from the viewpoint of classical isomorphism, the crystallochemical status of this form of occurrence of TE is rather vague: In this case the impurity does incorporate into the crystal structure (i.e., a mechanism of its incorporation on atomic level exists) but, chiefly, into its distorted sites situated within the range of action of elastic fields of dislocation clusters (first of all, dislocational walls that form interblock boundaries in the crystal). However, in the context of solid geochemistry, this is a natural consequence of interaction of elastic fields of point and linear defects, leading, under favorable conditions, to incorporation of some additional atoms of the dopant into a real crystal structure [2]. Thus, the case analyzed is closer to the concept of endocrypty [12] as the phenomenon of location of dopant atoms in the real structure of the host crystal. Note that this approach removes the logical contradiction in the concept of "isomorphous mixture" in which one of the components does not exist in a pure form (is imaginary). This component becomes real under conditions of a real crystal, say, in the structure sites distorted by elastic fields of defects, where principally it can form its own phase (in the limit, near the core of dislocation). In addition, none of the models for solid solution can be adequate to the object when the factors governing endocrypty are ignored: We cannot a priori state that we deal with nothing else but an isomorphous mixture.

It is much more difficult to treat the first case (see Fig. 2, *a*). The difficulty arises from the fact that dislocations are nonequilibrium defects, whereas stoichiometric vacancies are in equilibrium (though vacancies can also be present in nonequilibrium concentrations [13]). This implies that introducing an additional factor of equilibrium (e.g., activity of component B in the gas phase giving the concentration of vacancies in sublattice A), we can consider this case as usual isomorphous substitution. Nevertheless, in the context of solid geochemistry, when the isomorphously substituting atom is considered a point defect of its crystal structure (along with vacancies and interstitial atoms) rather than a defect dissolved in the lattice of the host crystal, it is reasonable to refer this case to endocrypty as well. First, as said above, concentrations of own point defects in crystal may be nonequilibrium (the crystal itself may be in the state of forced equilibrium owing to interaction of vacancies [14]). Second, speaking about endocrypty in this definition, we do not place emphasis on the mutual substitution atoms (classical isomorphous substitution) and related energetic effects (heat of mixing), but we focus on the interaction of an impurity atom having its own elastic field (dilatation center) with elastic fields of other defects of the crystal (in the given case, stoichiometric vacancies).

Thus, this case is also to be considered in terms of endocrypty, which is more general as compared with the traditional concept of isomorphism, since it is valid for real crystals too. But if only equilibrium vacancies are under consideration, the methodology of experimental investigations has no principal differences from the common procedure: The crystal is saturated in the desired element at constant activity in the gas phase of the component that specifies the concentration of stoichiometric vacancies until this element forms its own phase. If this phase does not exist, the above-described method with SFC is used. We must take into account that the SFC can also interact with point defects and dislocations; therefore, we will need two types of extrapolation — according to the content of these defects and SFC concentration.

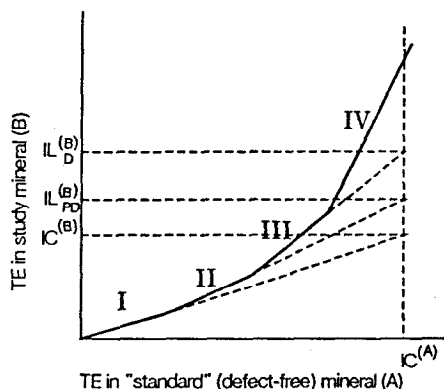


Fig. 3. A schematic distribution of a trace element between a hypothetical "standard" mineral and the mineral under study, containing only several types of defects of a crystal structure, with variable concentration of the saturation-favoring component. Phase correspondence in the system: I – real, II–IV – apparent.  $LC_{pd}$  – limiting concentration with participation of point defects (vacancies, interstitial atoms). The rest of the abbreviations follow Fig. 2.

### FORMS OF OCCURRENCE OF TRACE ELEMENTS

Of the factors limiting the method of study of TE behavior with the use of SFC, the hindered separation of different forms of occurrence of TE and isolation of a structurally bound form seem to be the most essential in the experimental and analytical context. In the TE saturation region of a mineral, as a rule, its several forms appear in crystals; the concentration of the structurally bound form may make up only a small part of the total content of TE. The use of SFC, which, by definition, must form quite stable complexes with TE, will inevitably lead to sorption of these complexes or their derivatives [9, 15]. Therefore, for both isomorphism (isodimorphism) and endocrypty, at least, three basic forms of TE occurrence should be distinguished – structural, sorptional, and properly mineral\*.

For sufficiently volatile elements (Hg, Cd, etc.) this possibility is provided by the method of thermal atomic absorption analysis [16, 17]. Unfortunately, for the majority of TE the problem is not solved in such a simple way. An original method is proposed in [15], which is based on special statistical treatment of the data obtained by analyzing a great number of individual crystals from each experiment for separating Au forms in minerals. The safe use of this method requires, however, close attention to the regions of the mineral that are undersaturated in TE. In this case, if we manage to match the mineral under study with a mineral having a sufficiently high solubility of TE, the principle of phase correspondence between the studied and chosen "standard" mineral (comparison mineral, after [15]) must hold in the region of undersaturation. Knowing the limiting concentration of TE incorporated into the comparison mineral, we can estimate it for the mineral under study as well. Using this method we managed to estimate the limiting concentration of Au incorporated into pyrite at 500 °C and 100 MPa at about 3 ppm (the literature data are rather contradictory). However, in the context of the preceding paragraph the approach described in [15] seems to be oversimplified. In fact, the cited work considers two lines of phase correspondence (PC) interpreted as lines of real and apparent PC (the latter is defined in [18]). But in the general case (see Fig. 2, a, b), there may be more lines of apparent PC (depending on the role of certain types of defects in TE endocrypty). Also, when we speak about apparent PC in sorptional forms, we must take into account that the adsorptional properties are often governed by the surface defects of growing crystals as well as by their growth rate and other factors [19]. Therefore, though the sorptional forms show a tendency toward a regular conjugated change in compositions of coexisting minerals owing to a similar reaction of these minerals to the growing content of TE in the fluid phase (apparent PC), we must take into account a possible ambiguity of this tendency, because there are too many difficult-to-control factors. By the way, two trends of PC have been established in [15] for pyrite and greenockite in distribution of Au in the domain of its contents beyond the limiting concentration incorporated into these minerals. As to the structural forms of TE (though bound with point defects and dislocations), we can be rather certain about apparent PC and change of distribution constant in comparison with real PC that belongs

\* This classification of TE forms is far from being arbitrary. In general, it corresponds to the known geochemical classification of trace elements by Shaw [1, p. 113].

to an actually isomorphous dopant.

The above is illustrated by Fig. 3, which is a diagram of phase correspondence of a system containing the above-mentioned mineral pair and a dopant element distributed in it. The abscissa is the TE content in a "standard" mineral containing no defects (in any case, those of them that significantly influence TE incorporation) and adopting TE into its structure only according to the scheme of classical isomorphism. The dashed line shows estimates of limited concentrations of incorporated TE for each of the forms but a sorptional one, to which the concept of limiting concentration in a similar sense is not applicable (the concept of sorptional capacity is quite uncertain, because it depends on many factors, see above). Figure 3 implies that in the case of endocrypty the limiting concentration under given  $P$  and  $T$  is not a constant but depends on what types of defects favor the incorporation of TE into the structure of a particular mineral. Thus, we again come to the conclusion that either experimentally or theoretically the answer should be found in the question which of the factors exert the most essential effect on the incorporation of TE into the crystal structure of the mineral.

## CONCLUSIONS

Regularities of precise sciences have still been used in geochemistry and mineralogy, ignoring the specific character of natural systems [20]. Therefore, investigators often encounter contradictions in behavior of elements and apparent neglect of their basic physicochemical laws. These laws evidently need adaptation to peculiarities of real mineral systems. An example may be the theory of forced equilibria [20], which permitted us to overcome a drawback in the use of chemical thermodynamics, which is restricted to mineral systems because of the inadequate presentation of the thermodynamic state of these systems. When real natural systems are examined by methods of chemical thermodynamics, modeling techniques are always subject to certain restrictions (e.g., method of minimization of thermodynamic potentials). Only in the case of completely equilibrated systems their study is restricted exclusively by the initial data precision, i.e., proceeds from thermodynamics itself. For the rest of the system types (locally equilibrated, partially equilibrated) the restrictions are either of empirical or kinetic nature. The concept of forced equilibria [21] recognizes a special type of systems in which restrictions of variations in the main (independent) or additional (inner) thermodynamic parameters are given by forcing factors. A particular kind of equilibrium conditions is determined by the type of forced equilibrium, which in turn is specified by the character of action of the forcing factor.

The concept of forcing equilibria is completely consistent with concepts of solid geochemistry [2]. As applied to trace elements, the consistence arises from the fact that the forcing factors are often related to structural imperfections (though not identical to them). This implies that in the context of the theory of forced equilibria it is possible to analyze the case when TE associated with structural defects incorporate into crystal in different forms.

Using the concept of endocrypty in its new interpretation as the phenomenon of disposition of atoms of an impurity in the real structure of the host mineral, we can adapt the known concepts of the limiting concentration of impurity and isomorphous capacity of mineral to structurally imperfect crystals. This is the first but necessary step; further improvements of the method proposed will permit us to model the endocrypty of trace elements with the help of the thermodynamical body of the theory of forced equilibria.

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