

ONCE AGAIN ABOUT ISOMORPHISM

Makarov V.P (The Russian State Geological Prospecting University)

litolog@msgpa.ru; ph.: (495) 433-56-77, add.: 11–38

Key words: *isomorphism, firm solutions*

Usually isomorphism is understood «as ability of elements to replace each other in crystal structures, not breaking their structure» [1]. The phenomenon of isomorphism opened still in XIX century (E.Micherlih, 1819), then developed by V.M. Goldshmidt, D.I. Mendeleyev, A.S. Fersman, V.I. Vernadsky, V.I. Lebedev, etc. researchers, is studied now thoroughly enough. This property of elements helped to understand many features of a structure and a chemical compound of minerals. At studying of concrete minerals were widely used various ideal schemes of isomorphic replacements,

On modern representations isomorphism is an ability of elements to form firm solutions [3]. As a rule, distinction between them consists that, speaking about isomorphism, we speak about behavior of pairs elements; speaking about firm solutions, we mean the connections formed by these elements, and elements are mineraloforming. The theory of hard solutions (THS) is developed full enough; THS has described behavior of pairs elements in various minerals and has established their degree isomorphophillen. So, the pair Mg - Fe is isomorphophillen in majority Fe-Mg-silicate and oxide minerals (biotites, garnets, olivines, pyroxenes, spinels) and forms in them almost ideal hard solutions. Therefore positions of the theory of hard solutions are used for the decision of practical problems, for example, for definition P-T of conditions of formation of minerals. At the same time the concept "isomorphism" has left on the second plan and has lost value what it had about 40 30 years ago.

Despite the reached successes in understanding of isomorphism, the analysis of great volume of results of practical applications of positions THS reveals two important lacks of these researches:

1. Absolutization of positions THS in the sense that they are applied without grounds enough, isomorphism always is supposed by default;
2. Absence of criteria of an estimation of existence of isomorphism in real natural minerals. There was not clear a question: whether always joint presence Mg and Fe^{+2} in the minerals specified above is spoken about display of isomorphic replacement by their friend the friend?

Replacement of one element by another occurs in crystallochemical cell; as parameter of cell C_{α} the full quantity of an element in a cell, or «formular weight» (on S.D. Chetverikovu, 1954) was accepted. For example, in olivine Mg_2SiO_4 there are cells «Mg» with parameter $C_{\alpha} = 2$ «Si» with $C_{\alpha} = 1$ etc. At replacement of an element the cell parameter always have to constants; for example, in olivine if there are no other replacements $Mg + Fe = 2$, or more generally $El_1 + El_2 = C_{\alpha}$. At presence in a cell of several elements - $\sum El_i = C_{\alpha}$. This condition also defines the basic method of the decision of a problem. Really, if only two elements - Mg also Fe-replace each other $Mg + Fe = C_{\alpha}$, hence in this binary system of concentration of elements are distributed on a straight line described by the equation of a kind, for example, $Mg = -Fe + C_{\alpha}$. Thus, in natural minerals for isomorphism definition performance of conditions is necessary: 1) parameters of elements should satisfy necessary conditions of isomorphic replacements (a necessary condition); 2) concentration of these elements in a mineral should be connected linear equation $El_1 = -El_2 + C_{\alpha}$ (a sufficient condition). Default of any of these signs allows to concern cautiously possibility of display of isomorphic replacements in real conditions.

As at the heart of job revealing of linear dependence prevalence of this dependence in minerals [4] was checked lays. Structures biotites, pyroxenes, garnets, olivines, spinels on literary data without division of minerals into kinds are analyzed. Homogeneous samples not only on minerals, but also on regions and breeds were made. Unfortunately, not all analyses are executed qualitatively, for example, for olivines; often there are no analyses on Fe^{+3} , Cr, Al. By results of chemical analyses are calculated crystallochemical factors, and then in each sample dependences of kind $El_1 = A(El_2) + In$ where El_1 and El_2 -crystallochemical factors of elements 1 and 2 were under construction. Together with it the invented communication Si - ^{IV}Al was not considered. For the further the analysis samples with $R^2 \geq 0.95$ are used.

Then the quantity of tests in sample was not less than 4. If $R^2 \geq 0.99$ samples with three tests were used. In the presence of communication between several elements samples in which this communication was established on the same tests were considered only. Some results of processing of tests are reflected in

tab. 1. In it N - total of the studied tests; N_c - total of tests in samples in which communication at least between two elements is found.

Table 1

	Pyroxenes		Biotites		Garnets	
N	1070		906		1232	
N_c	598		528		675	
ϕ	0.56		0.58		0.55	
	probes	extracts	probes	extracts	probes	extracts
Fe^{+2} -Mg	403/60.24	93/38.75	488/67.5	97/63.8	395/40.68	83/43.23
Fe^{+2} -Ca	299/44.69	67/27.92	52/7.2	13/8.6	190/19.57	44/22.92
Fe^{+2} -Na	86/12.86	13/5.42	15/2.1	6/4.0	0	0
Fe^{+2} -Mn	36/5.38	6/2.50	43/6	11/7.2	76/7.83	16/8.33
Fe^{+2} -Cr	3/0.45	1/0.42	0	0	60.62	1/0.52
Fe^{+2} -K	0	0	15/2.1	3.0/2/0	0	0
Mg- Ca	141/21.08	31/12.92	27/3.7	8/5.3	173/17.82	32/16.67
Al- Fe^{+3}	30/4.48	11/4.58	76/10.5	14/9.2	50/5.15	9/4.69
Al- Ca	23/3.44	6/2.50	0	0	0	0
Al- Mg	18/2.69	3/1.25	0	0	0	0
Al- Fe^{+2}	12/1.79	3/1.25	0	0	0	0
Al-Na	11/1.64	3/1.25	0	0	0	0
Al-Cr	5/0.75	1/0.42	0	0	81/8.34	7/3.65
Ca-Na	5/0.75	2/0.83	0	0	0	0
Σ	669/100	240/100	72/100	152/100	971/100	192/100

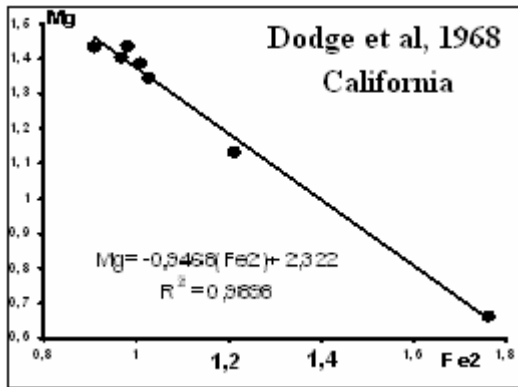


Fig.1. Distribution of concentration of a Fe^2 and Mg in biotites of granitoids

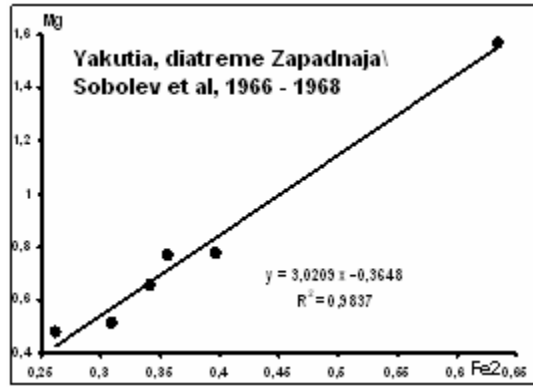


Fig.2. Distribution of concentration Fe^2 and Mg in garnets of grospydites

The relation $\phi = N_c/N$ characterizes the general connectivity of a mineral. In columns of "probes", "extracts" in numerator are resulted quantities of tests (general) in samples or extracts in which the given communication is revealed; in a denominator - their relative quantity in percentage. On **fig. 1 and 2** examples of behavior of elements in biotites and in garnets are resulted. The **table** reveals presence of certain laws. The size ϕ is approximately constant for all minerals and fluctuates within 0,55 0,58. Hence, half of tests does not participate in formation of isomorphic communications so presence in minerals of pairs isomorphic elements yet does not say that they are in a status of isomorphic replacement.

Most often there is pair Fe^{+2} - Mg, it is less - steams Fe^{+2} - Ca and Mg-Ca. It is clear, as specialized minerals are considered, and, hence, in them prevail Fe^{+2} and Mg. Calcium differences of minerals are rare enough. The obtained data allow considering pair Fe^{+2} - Mg as the main communication in these minerals and show very weak development of other communications.

2. Unlike the existing points of view in all minerals, except spineless, almost always there are no communications Al - Fe^{+3} , Al-Cr and Cr- Fe^{+3} . In spinels often enough there are communications Al - Cr, though all the same it is less (42,4 %), than communication Fe^{+2} -Mg (50 %). In single instances - communication Al- Fe^{+3} . In spineless there are also difficult communications of a kind $(\text{El}_1 + \text{El}_2) = f(\text{El}_3)$, for example:

1. Chromites (diatreme Mir): $\text{Fe}^{+3} = -0,7398(\text{Cr} + \text{Al}) + 1,478$; (summary from 18 tests);
2. Chromites (diatreme Ayhal): $(\text{Cr} + \text{Fe}^{+3}) = -0,9244\text{Al} + 1,968$ (9 tests) [5];
3. Unusual communications are revealed: Al - Ca, Al - Mg, Al - Fe^{+2} . The nature of these communications is not clear.
4. The analysis shows artificiality of some forms of heterovalency isomorphism: $\text{Si}^{+4} \rightarrow (\text{Al}^{+3} + \text{K}^{+1})$, $(\text{Ca}^{+2} + \text{Mg}^{+2}) \rightarrow (\text{Na}^{+1} + \text{Fe}^{+3})$ etc. The matter is that in these replacements elements K^{+} and Na^{+1} participate. **Feature** of these communications is that for full realization of free charges it is necessary to have commensurable concentration of elements. But in pyroxenes and garnets of concentration K^{+} and Na^{+1} so are small, that are not caught by the usual chemical analysis; it excludes possibility of realization of equivalent circuits. Revealing of these schemes on the basis of crystallochemical calculations is represented not convincing.

5. In general, two principal views of communications are allocated:

$\text{El}_1 = -\text{AEl}_2 + \text{V}$. On is in most cases characteristic for pairs Fe^{+2} -Mg, Fe^{+2} -Ca, Fe^{+2} -Mn, Mg - Ca, i.e. there were in the fullest measure isomorphic replacement of one element by another is shown. Besides it is established in systems of elements Al - Cr - Fe^{+3} (for example, resulted above the equation for spineless, sometimes biotites). It is revealed, that most the general is communication $\text{Mg} = -\text{AFe} + \text{V}$. She describes the overwhelming majority of distributions of elements in a wide range Fe - Mg - silicates. Having put $\text{M}_{\text{Fe}} = \text{M}_{\text{Mg}}$, we come to known expression $\text{Mg} = -\text{Fe} + \text{KK}_0$.

Communications of kind $\text{El}_1 = \text{AEl}_2 \pm \text{B}$.

In these conditions of concentration of elements vary simbasilly, as a first approximation it cannot be connected with isomorphism.

The carried out researches allow to draw following conclusions:

1. The basic criteria of revealing of isomorphic replacement in real natural systems (minerals): **and**. Elements (isomorphophillen) should possess the properties, allowing to carry out isomorphic replacement (a necessary condition); concentration isomorphophillen isovalency elements to are connected by equation $\text{El}_1 = -\text{AEl}_2 + \text{V}$. If any of these conditions are infringement it should be impossible to speak about presence of isomorphic replacement in real minerals.

2. The isomorphism phenomenon is not the essential factor of formation of a chemical compound of a mineral. Isomorphic replacement exists no more than in 50 % of minerals. In other cases there are other mechanisms of formation of a chemical compound of a mineral. The considerable part of schemes of isomorphism is decided and in real conditions on the named criteria does not prove to be true.

3. Three kinds of communication between steams of minerals which are described by the equations are allocated: $\text{El}_1 = -\text{AEl}_2 + \text{B}$; $\text{El}_1 = \text{AEl}_2 \pm \text{B}$. Sometimes equation $(\text{El}_1 + \text{El}_2) = f(\text{El}_3)$ comes to light the kind. Though second two equations pass one in another, however transition changes positions of elements, speaking about possible difference of these equations and a role of elements in formation of a chemical compound of a mineral.

References

1. Lazarenko E.K. Course of mineralogy. M: «Higher school», 1963.

2. *Urusov V. S.* The theory isomorphous miscibility. M: «Science», 1977.
3. *Makarov V.P.* «Equations of compensation»- a new method of studying petrochemical features of high-temperature formations (on an example of biotites). /Materials of meeting «Geochemistry, petrology, mineralogy and genesis of alkaline rocks». Miass: Institute of mineralogy of UrO of the RAN. 2006, P. 137-139.
4. *Makarov V.P.* Phenomenon of compensation - a new kind of communication between geological objects. In book: I International scientifically - practical conference «Formation of a modern science - 2006». Dnepropetrovsk: "Science and education", 2006. T.10. P.85 - 115. URL: <http://www.rusnauka.com/CCN/geographia/7-makarov.doc.htm>
5. *Sobolev N.V., Pohilenko N.P., Lavrentev J.G., et al.* Feature of chromsnelides structure from Yakutia diamonds and kimberlites. //J. Geology and geophysics, 1975. 11. P.7 - 24.

Electronic Scientific Information Journal "Vestnik Otdelenia nauk o Zemle RAN" № 1(27) 2009

ISSN 1819 – 6586

Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2009

URL: http://www.scgis.ru/russian/cp1251/h_dggms/1-2009/informbul-1_2009/mineral-13e.pdf

Published on July, 1, 2009

© Vestnik Otdelenia nauk o Zemle RAN, 1997-2009

All rights reserved