Towards an International Reference Environment of Chemical Exergy

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Abstract

The determination of the natural capital exergy is linked to the definition and thermodynamic properties of the Reference Environment (R.E.) used. Hence the importance of an appropriate selection of the R.E. The aim of this paper is to obtain, an agreement on the international reference environment for evaluating the natural resources on Earth. For this purpose, all the R.E. models published so far are systematically analyzed, the best suitable methodology for calculating the standard chemical exergy of the chemical elements is chosen and shown and the variables used in the chosen methodology are updated using new geochemical information and revisions done by other authors.

Key words: Reference Environment, Reference Substance, Standard Chemical Exergy, Natural capital

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1 Introduction

The natural capital can be evaluated from different points of view. One of them, and perhaps the most commonly known is the economic point of view. Nevertheless, as Naredo [1] analyzes, standard economy is only concerned with what which being directly useful to man, is also acquirable, valuable and produce-able. For this reason, most of the natural resources, remain outside the object of analysis of the economic system. The price-fixing mechanisms,

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rarely take into account the concrete physical characteristics which make them valuable. But natural capital has at least two physical features which make minerals or fresh water for example unusual: a particular composition which differentiates them from the surrounding environment, and a distribution which places them in a specific concentration. These intrinsic properties, can be in fact evaluated from a thermodynamic point of view in terms of exergy [2].

The thermodynamic value of a natural resource could be defined as the minimum work necessary to produce it with a specific structure and concentration from common materials in the environment. This minimum amount of work is theoretical by definition and is equal to the material's exergy (Riekert [3]). The exergy of a system gives an idea of its evolution potential for not being in thermodynamic equilibrium with the environment, or what is the same, for not being in a dead state related to the Reference Environment (R.E.). Therefore, for calculating the exergy of any natural resource, a R.E. should be defined. This R.E. must be determined by the natural environment and can be assimilated to a thermodynamically dead planet where all materials have reacted, dispersed and mixed.

Each of the R.E. definitions are fixed by their chemical composition. They have therefore different values of reference exergy and generate different exergies. This implies that the determination of the natural capital exergy is necessarily linked to the definition and thermodynamic properties of the R.E. Hence the importance of an appropriate selection of a R.E. for evaluating natural resources.

2 Searching the best suitable R.E. category

So far, there have been many contributions to the determination of a R.E. They could be divided into two main groups: *Partial* and *Comprehensive Reference Environments.*

It is well known, that some authors such as Bosnjakovich [4], Gaggioli and Petit [5] and Sussman [6] established that the R.E. should be defined according to the specific characteristics of the analyzed process. This criterion is based on that being the exergy a parameter that quantifies the theoretical evolution of a system with respect to the R.E., some of the possible evolutions of the system, cannot be attained because of process limitations. Hence, only possibilities of evolution that the system can practically attain are analyzed. The R.E. is not a "dead state" anymore. For computing exergy changes of variable composition or chemically reactive steady flow processes, a *Comprehensive Reference Environment* is generally unnecessary. However, this is not the case when the point is to evaluate the natural capital on Earth. In this case, there are no process limitations and the resources can follow an evolution process towards the dead state, thus a comprehensive R.E. is required.

Within the known *Comprehensive Reference Environments*, all authors agree in dividing the Reference Substances (R.S.) that compose the R.E. into gaseous components of the atmospheric air, solid components of the external layer of the Earth's crust, and molecular components of seawater. Nevertheless, there are also criterion differences between the different authors. They could be classified into environments based on 1) *Szargut's criterion*, 2) *Chemical equilibrium* and 3) *Abundance.*

Abundance and *Szargut's criterion* are not opposite criteria. According to *Szargut's criterion*, among a group of reasonable abundant substances, the most stable will be chosen if they also complain with the "Earth similarity criterion". That is, if the stability of the possible different reference substances for a specific element (measured in terms of the formation Gibbs energy) is within a certain threshold, then the most abundant R.S. will be chosen. If the differences exceed this threshold, the most stable substance will be taken as R.S. as long as it does not contradict the "Earth similarity criterion". The stability threshold has not a fix value and depends on each element considered, since it is subjected to geological uncertainties. Thus for example in the case of *Sb*, the substance Sb_2S_3 is more abundant than Sb_2O_5, nevertheless, according to *Szargut's criterion*, Sb_2O_5, which is much more stable, will be taken as reference substance. This happens also with the substances listed in table 1. Nevertheless nitrates such as $Ca(NO_3)_2$, $NaNO_3$, KNO_3 are discarded, because being most stable but not abundant in the natural environment, would break the similarity criterion if they are taken as R.S. Therefore, Szargut's [7] dead environment is similar to the real physical environment and should represent the products of an interaction between the components of the natural environment and the waste products of the processes. The most probable products of this interaction should be chosen as reference species. Next section explains purposively the well known Szargut's methodology for obtaining the chemical exergy of the elements from the R.E.

Some authors define the chemical exergy by means of the *chemical equilibrium* with the real environment. Szargut stresses that it is not possible to attain an equilibrium with the system being not in the state of internal equilibrium (and the natural environment is far away from such equilibrium). Ahrendts [8] and Diederichsen [9] for example, stated that if the amount of different elements in the reference system is known and the temperature of the system is fixed, the quantity of each chemical compound and the value of each chemical potential is uniquely determined by the condition of *chemical equilibrium.* Even though Ahrendt's R. E. only included 15 elements, they represented more than 99% of the Earth's crust and thus his R.E. can be considered as a *Comprehensive Reference Environment.* Ahrendts calculated the composition of this environment in chemical equilibrium, having as a variable parameter the thickness of the crust layer.

Valero, Ranz and Botero [2], explained already why Ahrendt's R.E. was not suitable to evaluate the natural capital on Earth. Most of the metals cannot be evaluated because they form part of the 1% of the Earth's crust neglected by Ahrendts. His obtained R.E. is very different from the real environment and it is very unlikely an eventual evolution towards it, since some processes are kinetically, biologically and/or geologically blocked.

Diederichsen updated and extended Ahrendt's model with new geochemical data and obtained among others, a R. E. including 75 elements. Furthermore, he allowed the composition of this environment to change with two variable parameters: thickness of the Earth's crust and ocean's depth. The final chosen environment should comply with the "Earth similarity criterion". The similarity with the Earth was measured with the equilibrium pressure, the oxygen and nitrogen content in the gas-phase and the equilibrium salt content in the oceans.

Even though Diederichsen [9] added more elements than Ahrendts [8] and included a new variable parameter, the composition of his new Reference Environment is still too different from the real Earth. According to the "Earth similarity criterion", the R.E. that best fits with the Earth's environment takes a crust thickness of only 0,1 m and an ocean's depth of 100 m. Greater values would move further away the R.E. from the real Earth, and would have among other features, reduced pressures and oxygen contents. As it happened with Ahrendt's model before, Diederichsen obtained high exergy values for oxygen. This happens because nearly all the oxygen of the air is consumed basically by the formation of nitrates and only in the limit, for a crust thickness of 0 m, the mean Earth pressure matches with that of the model. It seems therefore that achieving a R.E. in *chemical equilibrium* is in disagreement with the "Earth similarity criterion" and is not appropriate for the evaluation of natural capital on Earth. This idea fully fits with Lovelock's Gaia hypothesis [10]: the Earth is a life being and fights against thermodynamic stable equilibrium.

Kameyama et al. [11] proposed a reference environment with the criterion of chemical stability. The references are the most stable compounds among those with thermo-chemical data and can be integrated in the solid, liquid and gaseous environments. As Szargut stated in [12], some of the most stable compounds selected by Kameyama et al. like nitrates, compounds between rare elements (e.g. $PtBr_2$) or compounds with Fr as the reference species for the elements F, Cl, Br, I should not be recommended, because the probability of their formation in the environment is very small. Therefore, Kameyama et al. R.E. is not very suitable either to evaluate the scarcity of the natural capital.

According to Ranz [13], lots of minerals are compounds with the most common components of the upper continental crust, but are not very stable and do not represent the products of an interaction between the components of the natural environment and the waste products of industrial processes. Hence, Ranz [13] proposes a new R.E. very close to the real environment based on *abundance* and following *Szargut's criterion.* The solid phase of this new R.E. reproduces accurately the Earth's upper continental crust, since the solid reference species that make up this environment are the same as the most abundant types found in the Earth's upper continental crust. A problem with the Ranz proposed R.E. is that if we assign zero exergy to the most abundant substances, we are decreasing arbitrarily the natural capital, because many abundant minerals like sulfides naturally evolute to the most stable oxides. Therefore, as proposed by Valero, Ranz and Botero [2], we must return to Szargut's criterion of using the most stable substance, within the limits fixed by the "Earth similarity criterion".

Hence, our goal is to obtain an agreed legal international reference state for evaluating the natural resources on Earth, based on *Szargut's criterion* and methodology and using the more precise data used by Ranz and other authors such as Rivero [14], as well as new geochemical updates.

In the next section, Szargut's R.E. methodology is explained and the variables used are discussed.

3 Calculation methodology: standard chemical exergy of the chemical elements

Chemical exergy expresses the exergy of a substance at ambient temperature and pressure. It is defined as a maximum work which can be obtained when the considered substance is brought in a reversible way to the state of reference substances present in the environment, using the environment as a source of heat and of reference substances necessary for the realization of the described process. The R.S. most common in the environment are accepted separately for every chemical element, and are mutually independent. Hence, the problem of equilibrium between the reference substances does not exist. It is impossible to formulate a chemical reaction in which only the reference substances take part.

3.1 Standard chemical exergy of chemical compounds

3.1.1 Methodology

Standard chemical exergy results from a conventional assumption of a standard ambient temperature and pressure and standard concentration of reference substances in the natural environment.

The standard chemical exergy of any chemical compound can be calculated by means of the exergy balance of a reversible formation reaction;

$$b_{ch\,n} = \Delta G_f + \sum_e n_e \, b_{ch\,n\,e} \tag{1}$$

where:

ΔG_f	formation Gibbs energy
n_e	amount of kmol of the element e
$b_{ch\,n\,e}$	standard chemical exergy of the element.

If the chemical element does not belong to the reference substances, its standard chemical exergy can also be calculated from Eq. 1, however, a reference reaction of this element should be formulated. This reaction contains only reference substances, additional as reactants and final as products. For example, following reference reaction holds for the element C: $C+O_2 = CO_2$, where O_2 is the additional and CO_2 the final reference substance. The standard chemical exergy of the reference substances are calculated prior to the standard chemical exergy of the element.

3.1.2 Discussion of the variables used

The formation Gibbs energy used by Szargut [12] was revised by Rivero [14] using [15], [16], [17], [18] and [19]. No substantial differences were found, except for sillimanite (Al_2SiO_5), whose new value is $\Delta G_f = 2440,9$ kJ/mol. The information source of Ranz [13] for obtaining ΔG_f, was Faure [20], which is a compilation of the literature from several authors. This source corroborates Rivero's revision and thus, it will be considered for the calculation of our particular R.E.

3.2 Gaseous reference substances

3.2.1 Methodology

Free chemical elements present in the atmospheric air (O_2, N_2, Ar, He, Ne, Kr, Xe) and the compounds H_2O, CO_2 are assumed as reference substances. Their standard chemical exergy results from the conventional standard concentration in the atmosphere;

$$b_{ch\,n} = -RT_0 \ln \frac{P_{0n}}{P_n} = -RT_0 \ln z_0 \tag{2}$$

where:

R gas constant,

T_0 standard ambient temperature (298,15 K),

P_{0n} conventional mean ideal gas partial pressure in the atmosphere (kPa),

P_n standard pressure (101,325 kPa),

z_0 conventional standard molar fraction in the environment.

The values of standard chemical exergy of gaseous reference substances O_2, H_2O, CO_2, N_2 are calculated before other values because they are necessary in the calculation of standard chemical exergy of non-gaseous reference substances.

3.2.2 Discussion of the variables used

The universal gas constant is used (8,3143 kJ/(kmol K)) and the calculated standard chemical exergy relates to 1 kmol. Rivero and Garfias [14] accepted the reference pressure according to the conventional unit "physical atmosphere", thus 101,325 kPa. We are assuming the mean partial pressure calculated by Szargut and used by Ranz [13], which is the really appearing mean value and is equal to 99,31 kPa.

Table 2 shows the results obtained in this study for the chemical exergy of the gaseous substances. The obtained values are the same of those obtained by Szargut [12] and Valero, Ranz and Botero [2], since the methodology and the values used for this R.E. has been the same. The differences with Rivero and Garfias [14] are due to the different partial pressures in the atmosphere taken.

3.3 Solid reference substances

3.3.1 Methodology

For a prevailing part of chemical elements, solid R.S. commonly appearing in the external layer of the continental part of Earth's crust, have been assumed. However, the Earth's crust is a very complicated mixture of solid solutions and an exact calculation of the chemical exergy of its components is impossible. We can only approximately evaluate that exergy, assuming that the reference species behave as components of an ideal solution. Hence, Eq. 2 can be applied also in this case.

The evaluation of the standard molar concentration of solid R.S. in the external layer of the Earth's crust is difficult. In past geochemical publications we can only find a mean mass concentration of particular chemical elements and some information about the chemical compounds containing the considered elements. Hence, the best considered way so far to obtain the standard molar concentration of R.S. in the solid environment, has been with following equation suggested by Szargut in [12]:

$$z_{0\,i} = \frac{1}{l_i}\, n_{0\,i}\, c_i\, M_0 \tag{3}$$

where:

$n_{0\,i}$	mean molar concentration (in mol/kg) of the i-th element in the continental part of the Earth's crust,
l_i	number of the atoms of i-th element in the molecule of the reference species,
c_i	fraction of the i-th element appearing in the form of reference species,
M_0	mean molecular mass of the upper layer of the continental part of Earth's crust.

The reference reactions of the elements having solid R.S. contain usually the gaseous R.S. Sometimes appear also solid reference species. For example, the solid R.S. of Mg is $Mg_3Si_4O_{10}(OH)_2$ the reference reaction for the element Mg has a form:

$$3\ \mathrm{Mg} + 4\ \mathrm{Si}O_2 + 1{,}5\ \mathrm{O_2} + \mathrm{H_2O} = \mathrm{Mg_3Si_4O_{10}(OH)_2}$$

In such case the standard chemical exergy of the appearing solid reference substance should be calculated prior to the calculation of the chemical exergy of the considered element.

3.3.2 Discussion of the variables used

The mean molar concentration of the elements in the upper continental crust n_{0i}, used in Szargut [12], was the recommended by Polanski and Smulikowski [21]. Ranz [13] used updated values mainly from Taylor and McLennan [22], [23]. For the elements: Br, C, Cl, F, S, Pt, Pu, Ra, Rh, Ru, Te, I, Hg and N, Taylor and Mclennan did not provide any information, therefore, Ranz used the values given by Wedepohl [24] for S, Br, C, F, I, Hg, N and for the remainig elements, the values used by Szargut [12]. Some authors like Plank and Langmuir [25] basing on their studies on marine sediments, suggested already in 1998 some revisions of the estimated values by Taylor and McLennan [22], [23] for Nb, Cs, Ti, Ta. As a consequence, McLennan [26] published in year 2001 new mean molar concentrations of the upper continental crust for the elements: Sc, Ti, V, Co, Ni, Nb, Cs, Pb, Ta. Grigor'ev published in year 2000 [27] the average mineral content of the upper continental crust obtained through a great number of quantitative mineralogical analysis of important rocks published mainly in the USSR and USA. Recently, Grigor'ev updated this information; this new analysis comprises 255 minerals corresponding to 99,13% of the total mineral content of the upper continental crust. Although Grigor'ev has not published this information yet, he gave permission to the authors of this paper, to use it. This valuable information will allow to obtain directly the standard molar concentration of the following 12 reference substances in the solid environment without using Eq. 3: $BaSO_4$, $CaCO_3$, Au, Fe_2O_3, $Mg_3Si_4O_{10}(OH)_2$, MnO_2, SiO_2, $SrCO_3$, ThO_2, SnO_2, TiO_2, $ZrSiO_4$. For the rest substances, Eq. 3 must be used, taking n_{0i} from the latest geochemical publications. First the values from McLennan [26] completed with those from Wedepohl [24] will be used. For the remaining elements not appearing in the latter publications, n_{0i} used by Szargut [12] will be applied.

The mean molecular mass of the upper layer of the continental part of the Earth's crust, was first estimated by Szargut [28]. The obtained value was M_0= 135,5 kg/kmol, applying the following estimation method: according to the geochemical data, the mean concentration values (in mol/kg) of particular chemical groups or elements in the external layer of the continental Earth's crust and the chemical compound formed from these groups were assumed. The first considered group was CO_2, which appears in the Earth's crust mainly in carbonates of Ca, Mg and Fe. Per 1 mol of (CaO + MgO + FeO) 0,035 mol of CO_2 are present. The group CO_2 was partitioned between the mentioned groups and elements Zn, Cu, Pb and Cd, appearing also in the form of carbonates. The group SO_3 was partitioned between CaO and MgO forming sulphates. It was assumed that a prevailing part of metals (Sn, Co, Mn, Fe, Ni) appears in form of different oxides (Co_2O_3, Co_3O_4, Fe_2O_3, Fe_3O_4). It was also assumed that 8% of Fe appears in form of free oxide Fe_2O_3. The remaining part appears in form of $FeTiO_3$, $FeCr_2O_3$ and silicates. For example, following silicates were assumed: $NaAlSi_3O_8$, $KAlSi_3O_8$, $NaFeSi_2O_6$, $MgSiO_3$,

$CaO.Al_2Si_2O_7$. Because of the large content of SiO_2, a considerable part of it was assumed in free form. After estimating the composition of a mean sample of the lithosphere, its molecular mass was calculated.

Ranz [13] updated the molecular mass of the upper continental crust using more recent geochemical information and adopting not only a geochemical approach, but also a geological one. The methodology used was as follows: The international accepted norm CIPW [29] was applied to the mass fractions of the principal oxide groups obtained by Carmichael [30] for the cratonic and sedimentary layers, in order to redistribute the chemical components from the oxides to the mineral molecules that are representative in real minerals appearing in a rock. Next, the minerals of the norm and their respective relative masses were modified to adjust them to the real volumes of the principal groups of each rock. Finally, their molar fractions were calculated and the mean molecular mass of the whole was obtained. The resulting M_0 was equal to 145,5 kg/kmol. Even though this methodology used better geochemical values than the ones in Szargut [28], and included the geological approach, we cannot forget that the CIPW norm is an artificial way to obtain the possible minerals that can appear in a rock. It is therefore only an approximation as well.

In the light of Grigor'ev's analysis, a more accurate molecular weight of the upper continental crust, based on experimental results rather than assumptions, can be easily obtained. The new calculated value is M_0= 143,4 kg/kmol, which is very close to the estimation done by Ranz. The difference in the chemical exergy of the elements obtained with the new molecular weight is almost negligible: in average, taking a molecular weight equal to 143,4 instead of 145,5, makes a difference in the exergy of the solid reference substances of only 0,007%.

For the fraction of the i-th element appearing in the form of reference species (coefficient c_i), Szargut [31] associates values comprised between 0,5 for more abundant substances and 0,001 for less frequent substances from geochemical data given by Polanski and Smulikowski [21]. Ranz [13] obtained more accurate c_i coefficients for solid R.S. containing the most abundant elements in the upper continental crust. For this purpose, she used the mineralogical composition of the Earth's upper layer obtained with the CIPW norm before and updated geochemical information, mainly from Taylor and McLennan [23]. For minority elements, due to the lack of information, Szargut's [31] values were used. As long as a better mineralogical composition of the Earth's crust is done and the c_i coefficients are recalculated with this information, we will assume the c_i values obtained by Ranz [13]. Nevertheless, it must be stressed that choosing a certain c_i or another a 100 times greater, throws less differences in the chemical exergy of the elements than choosing another R.S.

Tables 4 and 5show the results obtained in this study for the chemical exergy of the solid substances. The solid R.S. assumed were those taken by Szargut [12], basing on the *Szargut's criterion* mentioned before. The new chemical exergies obtained differ in 1,1% in average with respect to the values obtained by Szargut in [12]. Taking the empirical standard molar concentration of solid R.S. found in Grigor'ev [27] instead of calculating it with Eq. 3, implies a difference in the element chemical exergy of less than 4% except for Au (14%) and F (18%). For the latter elements, the greater difference is due to the greater sensitivity of Au to z_0, since its ΔG is equal to zero and the great proportion of atoms of Ca in the reference substance of F, respectively.

3.4 Reference substances dissolved in seawater

3.4.1 Methodology

Assumption of ionic or molecular R.S. dissolved in seawater ensures in many cases more exact determination of standard chemical exergy of chemical elements when compared with solid R.S. The calculation methods of thermodynamic functions of monocharged and bicharged ions are relatively exact. This is the case also when the reference substance is dissolved in molecular form with a very small degree of ionization.

The method of calculation of standard chemical exergy of elements with R.S. dissolved in seawater has been developed by Morris [32]:

$$b_{ch\,n} = j\Big(-\Delta\, G_f + 0.5\, z\, b_{ch\,H_2} - \sum_k \nu_k\, b_{ch\,k} - R\, T_n\, [2.303\, z\, (pH) + \\ + \ln\, m_n\, \gamma]\Big) \qquad (4)$$

where:

j	number of reference ions or molecules derived from one molecule of the element under consideration,
ΔG_f	formation Gibbs energy of the R.S.,
z	number of elementary positive charges of the reference ion,
ν_k	number of molecules of additional elements present in the molecule of reference substance,
$b_{ch\,H_2}, b_{ch\,k}$	standard chemical exergy of hydrogen gas and of the k-th additional element.
m_n	conventional standard molarity of the reference substance in seawater,
γ	activity coefficient (molarity scale) of the reference substance in seawater,
pH	exponent of the concentration of hydrogen ion in seawater (=8,1)

The activity coefficient of single ion can be calculated by means of the Debye-Huckel equation:

$$-\log\gamma_i = \frac{A\, z_i^2 \sqrt{I}}{1 + a_i\, B \sqrt{I}} \tag{5}$$

where:

A = 0,51 $\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$ for water at 25^{o}C,

B = 3,287 * 10^9 $\mathrm{kg}^{1/2}\,\mathrm{m}^{-1}\,\mathrm{mol}^{-1/2}$ for water at 25^{o}C,

a_i effective diameter of the ion,

I ionic strength of the electrolyte.

The ionic strength of the electrolyte results from the following equation:

$$I = \frac{1}{2}\sum_i m_i\, {z_i}^2 \tag{6}$$

where:

m_i molarity of the ion, mol/kg H_2O,

z_i number of elementary electric charges of the ion.

The ion Cl^- prevails among the negative ions in seawater. Therefore, the data of chlorides can be assumed for activity coefficients of the positive ions Na^+, K^+. The activity coefficients of the negative ions Cl^- and SO_4^{-2} can be estimated in reference to the predominant positive ion Na^+.

3.4.2 Discussion of the variables used

The positive ionic R.S. have been assumed for the elements from the first column of the periodic system and for the monocharged and bicharged negative ions formed from acids. The elements from the second column of the periodic system appear in the seawater in form of positive bicharged ions, however, they are not recommended as R.S., because the so calculated standard chemical exergy of the elements leads to negative values of chemical exergy of some solid compounds common in the Earth's crust. Rivero and Garfias [14] have found the influence of salinity of seawater on the calculated values of standard chemical exergy of elements calculated by means of reference substances dissolved in seawater. However, an increased salinity (greater than 35‰ appears seldom (Red Sea), and the deviations are not large (usually less than 1,6%). Every introduction of solid reference substances can decrease the accuracy of calculations. Therefore we are assuming the solid reference substances only for the elements from the second column of the periodic system. Following ionic and molecular reference substances dissolved in seawater have been accepted in the recent publication of Szargut [33] and will be used for this proposal:

Cl^-, $AgCl_2^-$, $B(OH)_3$ aq, BiO^+, Br^-, $CdCl_2$ aq, Cs^+, Cu^{+2}, HPO_4^{-2}, $HAsO_4^{-2}$, $HgCl_4^{-2}$, IO_3^-, K^+, Li^+, MoO_4^{-2}, Na^+, Ni^{+2}, $PbCl_2$ aq, Rb^+, SO_4^{-2}, SeO_4^{-2}, WO_4^{-2}, Zn^{+2}.

Major ions in seawater are ions with fractions greater than 1 ppm. The Seawater Reference Environment taken into account in this proposal comprises the following major ions: Na^+, K^+, $HAsO_4^{-2}$, BiO^+, Cl^-, SO_4^{-2}, Br^-, $B(OH)_3$. Values of the activity coefficients and molarity of these species basing on information presented in Millero [34], Pilson [35] and Mottl [36] were reviewed and compared with those which Ranz and Rivero took into account. With the exception of SO_4^{-2} the differences are negligible from the point of view of the influence on the final exergy of the considered element. In case of SO_4^- Szargut and Ranz assumed a value of m = 1,17E-2, and Rivero m = 1,24E-2. The molarity calculated basing on the three independent sources [34], [35] and [36] is estimated as m = 2,93E-2 and is almost 2,5 times greater. This difference decreases the chemical exergy of sulfur only about 2 kJ/mol. The rest of the obtained results are very similar to previous investigations and the differences are negligible.

Table 3 shows the results obtained in this study for the chemical exergy of the substances dissolved in seawater.

4 Conclusions

A revision of the different R.E. proposed so far has been done. The authors have agreed to choose as best suitable R.E. category for the evaluation of natural capital, a *Comprehensive Reference Environment* based on *Szargut's criterion*. The parameters used in the equations for calculating the chemical exergy of the elements, mainly ΔG, n_0, M_0, c_i, z_{0i} and m, have been revised and updated according to new geochemical information and revisions done by other authors. It has been stated, that the differences on the chemical exergies of the elements between the different authors is not very significant. Therefore, the current authors proposed in ECOS 2005 conference, to take the agreement of accepting internationally the R.E. presented in this paper for the evaluation of the exergy resources on Earth. Nevertheless, it has been seen, that this information can be further improved if more empirical updates appear. Presently, the authors of this paper are working on improving the data, but other interested authors are invited to join this research.

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Table 1
Exergy difference of selected elements considering either as reference species the most abundant or the most stable substances in the R.E. [2]

Element	**Most abundant species**	**Most stable species**	**Exergy difference, kJ/mol**
Sb	Sb_2S_3	Sb_2O_5	1235,58
As	FeAsS	As_2O_5	1201,32
S	FeS_2	$SO4^{-2}$	963,63
Bi	Bi	BiO^+	228,88
Cd	CdS	CdCl2	745,75
Ce	$CePO_4$	CeO_2	258,33
Zn	ZnS	Zn^{+2}	717,22
Co	Co_3S_4	Co_3O_4	967,7
Cu	$CuFeS_2$	Cu^{+2}	1423,18
Mo	MoS_2	MoO_4^{-2}	1675,9
Os	Os	OsO_4	306,81
Ag	Ag_2S	$AgCl_2^-$	330,65
Pt	Pt	PtO_2	84,59
Pb	PbS	$PbCl_2$	710,34
Re	ReS_2	Re_2O_7	1556,65
Ru	Ru	RuO_2	254,82
U	UO_2	$UO_3.H_2O$	127,49

Table 2
Chemical exergies of the elements for gaseous reference substances

ELEM.	**REFERENCE SPECIES**				**CHEMICAL ELEM. EXERGY, kJ/mol**				
Element	**Formula**	P_{0n}, **kPa**	**Chemical exergy, kJ/mol**	**ΔGf, kJ/mol**	**State**	**This proposal**	**Szargut 1989**	**Valero et al. 2002**	**Rivero and Garfias 2004**
Ar	Ar	9,06E-03	11,69	0	g	**11,69**	11,69	11,69	11,64
C	CO_2	3,35E-04	19,87	-394,36	s.,graf.	**410,25**	410,26	410,26	410,27
H	H_2O	2,20E-02	9,49	-228,59	H_2,g	**236,10**	236,1	236,10	236,12
He	He	4,85E-06	30,37	0	g	**30,37**	30,37	30,37	31,31
Kr	Kr	9,70E-07	34,36	0	g	**34,36**	34,36	34,36	34,30
Ne	Ne	1,77E-05	27,16	0	g	**27,16**	27,16	27,16	27,14
N	N_2	7,58E-01	0,72	0	N_2, g	**0,72**	0,72	0,72	0,67
O	O_2	2,04E-01	3,97	0	O_2, g	**3,97**	3,97	3,97	3,92
Xe	Xe	8,70E-08	40,33	0	g	**40,33**	40,34	40,33	40,27

Table 3
Chemical exergies of the elements for aqueous reference substances

ELEM.	**REFERENCE SPECIES**						**CHEMICAL ELEM. EXERGY, kJ/mol**			
Element	**Formula**	**z**	γ	m_n, **mol/kg**	**ΔGf, kJ/mol**	**State**	**This proposal**	**Szargut 1989**	**Valero, Ranz and Botero 2002**	**Rivero and Garfias 2004**
Ag	$AgCl_2^-$	-1	0,6	2,70E-09	-215,5	s	**69,85**	70,2	70,28	lithosph.
As	$HAsO_4^{-2}$	-2	0,138	2,10E-08	-714,7	s	**493,83**	494,6	lithosph.	492,60
B	$B(OH)_3$	0	1	3,40E-04	-968,8	s	**628,60**	628,5	628,49	628,10
Bi	BiO^+	1	0,52	1,00E-10	-146,4	s	**274,92**	274,5	274,56	274,80
Br	Br^-	-1	0,73	8,70E-04	-104,0	Br_2, l	**100,89**	101,2	101,25	101,00
Cd	$CdCl_2$	0	1	6,90E-11	-359,4	s	**293,37**	293,8	293,8	lithosph.
Cl	Cl^-	-1	0,63	5,66E-01	-131,26	Cl_2, g	**124,03**	123,6	123,66	123,70
Cs	Cs^+	1	0,6	2,30E-09	-282,2	s	**404,58**	404,4	404,58	404,60
Cu	Cu^{+2}	2	0,2	7,30E-10	65,5	s	**134,25**	134,2	134,24	lithosph.
Hg	$HgCl_4^{-2}$	-2	0,1	3,40E-10	-446,9	l	**114,99**	115,9	115,86	lithosph.
I	$IO3^-$	-1	0,6	5,20E-07	-128,0	I_2, s	**174,74**	174,7	174,76	175,70
K	K^+	1	0,62	1,06E-02	-282,4	s	**366,66**	366,6	366,67	366,7
Li	Li^+	1	0,68	2,50E-05	-294,0	s	**393,03**	393,0	393,03	392,7
Mo	MoO_4^{-2}	-2	0,1	1,10E-07	-836,4	s	**730,27**	730,3	730,29	731,3
Na	Na^+	1	0,65	4,86E-01	-262,05	s	**336,71**	336,6	336,66	336,7
Ni	Ni^{+2}	2	0,2	1,20E-07	-45,6	s	**232,70**	232,7	232,7	lithosph.
P	HPO_4^{-2}	-2	0,1	4,90E-07	-1089,3	s	**861,42**	861,4	861,43	861,3
Pb	$PbCl_2$	0	1	4,20E-11	-297,2	s	**232,40**	232,8	232,83	lithosph.
Ru	Rb^+	1	0,6	1,40E-06	-282,4	s	**388,89**	388,6	388,88	388,7
Se	SeO_4^{-2}	-2	0,1	1,20E-09	-441,4	s	**346,47**	346,5	346,49	347,5
S	SO_4^{-2}	-2	0,11	2,93E-02	-744,6	s	**607,05**	609,6	609,56	609,3
W	WO_4^{-2}	-2	0,1	5,60E-10	-920,5	s	**827,46**	827,5	827,48	828,5
Zn	Zn^{+2}	2	0,2	1,70E-08	-147,3	s	**339,25**	339,2	339,24	lithosph.

Table 4
Chemical exergies of the elements for solid reference substances (1)

ELEMENT		**REFERENCE SPECIES**						**CHEMICAL ELEM. EXERGY, kJ/mol**			
Elem.	**noi, mol/g**	**Formula**	**ci**	**z0**	**Chemical exergy, kJ/mol**	**ΔGf, kJ/mol**	**State**	**This proposal**	**Szargut 1989**	**Valero et al. 2002**	**Rivero and Garfias 2004**
Al	2,98E-03	Al_2SiO_5	0,01	2,14E-01	3,83	-2440,9	s	**796,10**	888,20	RS = Al2O3	795,7
Au		Au		3,23E-11	59,88	0	s	**59,88**	50,5	53,39	50,6
Ba		$BaSO_4$		5,88E-06	29,85	-1361,9	s	**776,76**	775,1	774,25	775,4
Be	3,33E-07	Be_2SiO_4	0,01	2,39E-07	37,80	-2033,3	s	**604,53**	604,40	RS = BeO	604,3
Ca		$CaCO_3$		5,48E-04	18,61	-1129	s	**731,40**	729,10	hydrosph.	729,1
Ce	4,57E-07	CeO_2	0,02	1,31E-06	33,58	-1024,8	s	**1054,40**	1054,60	1054,38	1054,7
Cr	1,60E-06	$K_2Cr_2O_7$	0,01	1,15E-06	33,91	-1882,3	s	**584,49**	584,3	RS = Cr2O3	584,4
Co	2,89E-07	$CoFe_2O_4$	0,005	2,07E-07	38,15	-1032,6	s	**308,82**	312,00	RS = Co3O4	313,4
Dy	2,15E-08	$Dy(OH)_3$	0,02	6,17E-08	41,15	-1294,3	s	**975,35**	975,9	975,32	976
Er	1,38E-08	$Er(OH)_3$	0,02	3,96E-08	42,25	-1291	s	**973,15**	972,8	973,12	972,8
Eu	5,79E-09	$Eu(OH)_3$	0,02	1,66E-08	44,41	-1320,1	s	**1004,40**	1003,8	1004,37	1003,8
Fl	3,30E-05	CaF_2*3$Ca_3(PO)_2$	0,01	2,37E-05	26,40	-12985,3	F_2,g	**481,54**	504,90	RS = CaF2	505,8
Gd	1,93E-08	$Gd(OH)_3$	0,02	5,54E-08	41,42	-1288,9	s	**970,22**	969	969,63	969
Ga	2,44E-07	Ga_2O_3	0,02	3,50E-07	36,85	-998,6	s	**514,75**	514,9	514,73	515
Ge	2,20E-08	GeO_2	0,05	1,58E-07	38,83	-521,5	s	**556,35**	557,6	556,33	557,7
Hf	3,25E-08	HfO_2	0,05	2,33E-07	37,86	-1027,4	s	**1061,28**	1062,90	1061,26	1063,1
Ho	4,85E-09	$Ho(OH)_3$	0,02	1,39E-08	44,85	-1294,8	s	**979,54**	978,6	979,51	978,7
In	4,36E-10	In_2O_3	0,05	1,56E-09	50,26	-830,9	s	**437,60**	436,8	437,59	436,9
Ir	1,04E-13	IrO_2	0,005	7,46E-14	74,93	-185,6	s	**256,56**	246,80	256,53	247
Fe		Fe_2O_3		7,78E-04	17,75	-742,2	s	**376,99**	374,8	374,81	374,3
La	2,16E-07	$La(OH)_3$	0,02	6,19E-07	35,43	-1319,2	s	**994,53**	994,6	994,5	994,7
Lu	1,83E-09	$Lu(OH)_3$	0,02	5,25E-09	47,26	-1259,6	s	**946,76**	945,7	946,73	945,8
Mg		$Mg_3Si_4 O_10(OH)_2$		1,75E-04	21,45	-5543	s	**629,37**	626,1	hydrosph.	626,9
Mn		MnO_2		6,81E-07	35,20	-465,2	s	**496,42**	482	482,93	487,7
Nd	1,80E-07	$Nd(OH)_3$	0,02	5,16E-07	35,89	-1294,3	s	**970,08**	970,1	970,05	970,1
Nb	1,29E-07	Nb_2O_3	0,01	9,25E-08	40,15	-1766,4	s	**900,29**	899,7	899,37	899,7
Os	2,63E-13	OsO_4	0,005	1,89E-13	72,63	-305,1	s	**369,78**	368,1	369,76	368,4
Pd	4,70E-12	PdO	0,005	3,37E-12	65,48	-82,5	s	**146,00**	138,6	145,97	138,7
Pt	2,60E-11	PtO_2	0,005	1,86E-11	61,24	-83,7	s	**140,97**	141	140,9	141,2
Pu	6,20E-20	PuO_2	0,01	8,89E-20	108,74	-995,1	s	**1099,87**	1100	1099,84	1100,1
Pr	5,04E-08	$Pr(OH)_3$	0,02	1,45E-07	39,04	-1285,1	s	**964,04**	963,8	964,01	963,9
Ra	4,40E-15	$RaSO_4$	0,05	3,15E-14	77,06	-1364,2	s	**826,27**	823,9	823,69	824,2
Re	2,15E-12	Re_2O_7	0,01	1,54E-12	67,42	-1067,6	s	**560,56**	559,5	560,27	559,6

Table 5
Chemical exergies of the elements for solid reference substances (2)

ELEMENT		**REFERENCE SPECIES**						**CHEMICAL ELEM. EXERGY, kJ/mol**			
Elem.	**noi, mol/g**	**Formula**	**ci**	**z0**	**Chemical exergy, kJ/mol**	**ΔGf, kJ/mol**	**State**	**This proposal**	**Szargut 1989**	**Valero et al. 2002**	**Rivero and Garfias 2004**
Rh	9,70E-12	Rh_2O_3	0,005	3,48E-12	65,41	-299,8	s	**179,62**	179,7	176,61	179,7
Ru	1,00E-12	RuO_2	0,005	7,17E-13	69,32	-253,1	s	**318,45**	318,6	318,42	318,6
Sb	1,64E-09	Sb_2O_5	0,001	1,18E-10	56,68	-829,3	s	**438,02**	438,01	438,01	438,2
Sc	3,03E-07	Sc_2O_3	0,05	1,09E-06	34,04	-1819,7	s	**923,89**	925,2	924,14	925,3
Si		SiO_2		5,75E-01	1,37	-856,7	s	**854,10**	854,9	854,18	855
Sm	2,99E-08	$Sm(OH)_3$	0,02	8,58E-08	40,34	-1314	s	**994,23**	993,6	994,2	993,7
Sn		SnO_2		2,87E-08	43,05	-519,6	s	**558,67**	551,9	549,15	551,8
Sr		$SrCO_3$		1,96E-09	49,71	-1140,1	s	**773,59**	749,8	748,63	749,8
Ta	5,53E-09	Ta_2O_5	0,01	3,97E-09	47,96	-1911,6	s	**974,81**	974	973,82	974,1
Te	1,40E-11	TeO_2	0,005	1,00E-11	62,78	-270,3	s	**329,10**	329,2	329,08	329,3
Tb	4,03E-09	$Tb(OH)_3$	0,02	1,16E-08	45,30	-1314,2	s	**999,40**	998,4	999,37	998,5
Tl	3,67E-09	Tl_2O_4	0,01	2,63E-09	48,97	-347,3	s	**194,16**	194,9	194,15	194,9
Th		ThO_2		1,86E-10	55,54	-1169,1	s	**1220,67**	1202,6	1202,09	1202,7
Tm	1,95E-09	$Tm(OH)_3$	0,02	5,59E-09	47,10	-1265,5	s	**952,50**	951,7	952,47	951,8
Ti		TiO_2		1,99E-04	21,13	-889,5	s	**906,65**	907,2	902,89	907,2
U	1,18E-08	$UO_3.H_2O$	0,01	1,69E-08	44,36	-1395,9	s	**1196,22**	1196,6	1196,19	1196,6
V	2,10E-06	V_2O_5	0,01	1,51E-06	33,23	-1419,6	s	**721,45**	720,4	722,15	721,3
Yb	1,27E-08	$Yb(OH)_3$	0,02	3,64E-08	42,46	-1262,5	s	**944,85**	944,3	944,83	944,3
Y	2,48E-07	$Y(OH)_3$	0,02	7,11E-07	35,09	-1291,4	s	**966,39**	965,5	966,37	965,6
Zr		$ZrSiO_4$		7,88E-05	23,42	-1919,5	s	**1080,88**	1083,4	RE = ZrO2	1083