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New method to compute the emergy of crustal minerals

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ABSTRACT

To date, Unit Emergy Values (UEVs) for crustal minerals (e.g. limestone, iron ore, etc.) have lacked thermodynamic basis and suffer from overly vague generalization (relative to most other, more certain emergy indicators). We assume a steady state crustal cycle that embodies the various forms of exergy supporting Earth system cycles. The UEV of average crust is 1.75E + 09 solar emergy joules per gram (specific emergy). The ratio of crustal specific emergy to a mineral's exergy density (exergy per mass) is the mineral's transformity. This is an important assertion as it is the dissipation of exergy which hierarchically organizes materials. Emergy accounting should be able to express every resource either a transformity or specific emergy, linked by exergy density; crustal minerals are no exception.

Mineral transformity can be characterized using either chemical exergy or Gibb's formation energy. Both calculations use the same mixing term which depends on average crustal abundance of the mineral. Also it's possible to account mineral emergy using either total free energy (or total chemical exergy) or by accounting only the mixing exergy. Four herein proposed methods yield a wide range of specific emergies for each of the prominent mineral/metal inputs to economies. We conclude that the exergy of concentration (mixing exergy) best represents that which is destroyed in mining/extraction activities and that using Gibb's transformities better suit the emergy method due to chemical exergies being positive or negative depending on the mineral. The emergy accounting of minerals should utilize Gibb's transformities and account only the emergy of a mineral's mixing exergy because this represents the natural capital that is irrevocably destroyed in mineral harvesting.

1. Introduction

Exergy means *available potential energy*. Exergy is "the amount of work obtainable when some matter is brought to thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interaction only with the above-mentioned components of nature" (Szargut et al., 1988). Emergy is a measure of all degraded exergy, from a predefined time origin, which contributed to generating a 'given system' under consideration (Giannantoni, 2002).

Sunlight is the most practical unit for emergy because it's the most abundant and evenly distributed exergy source to the Earth system. Thus Earth emergy is expressed as solar emergy joules (seJ). The two other important independent exergy sources to the Earth are deep earth heat and the gravitational potential energy of the Earth-Moon-Sun system. This tripartite of exergy sources are expressed as equivalent sunlight exergy based on their joint work accomplished in the steady state geobiosphere (Brown and Ulgiati, 2010). The sum of the tripartite is the geobiosphere emergy baseline (GEB; 15.2 $E + 24$ seJ/yr).

When concentrated materials disperse to ambient abundances, heat and entropy are generated (Faber, 1984). A concentration gradient is thus a storage of available potential energy (a.k.a. exergy). The cumulative exergy of one form dissipated to create a concentration gradient is the gradient's emergy. The ratio of this gradient's emergy to its exergy is named transformity (seJ/J). Transformity offers a hierarchical perspective of energy quality (Giannantoni, 2002) in the geobiosphere. Quality indicates the donor-, or supply-side perspective (i.e. what is required from the environmental for genesis) of an exergy's ability to induce useful work (utility) in the geobiospheric system (Odum, 1996). A storage's emergy divided by its useful mass is called specific emergy (seJ/g). Specific emergy indicates material quality and is linked to transformity via specific exergy (J/g). Specific emergy and transformity, by definition, jointly characterize resource quality. They are collectively referred to as UEVs (unit emergy values).

Abbreviations: Ga, Giga-annum, i.e. one billion years; GEB, geobiospheric emergy baseline; ME, mass enrichment method; NEAD, National Emergy Accounting Database; RE, reference environment; UEV, unit emergy value.

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A driving question for this research is how to relate crustal mineral specific emergy to changes in concentration *and* changes in specific exergy? Presently crustal material emergy is accounted by mass, rather than by exergy, because accounting mass is more familiar and more common in the emergy literature, and mass is easier to handle with available computation methods. Flaws of these methods will be discussed, after which we present the calculation procedure to produce unique UEVs for crustal minerals. Lastly we apply these new UEVs to the emergy accounting of the US mineral consumption in 2008, and compare the results with previous analyses.

1.1. Previous estimates of crustal mineral emergy

Various tectonic (Odum, 1996; Table 3) and sedimentary processes (Odum, 2000a; Table 1) were evaluated as co-products of the GEB. Co-product assumption is like a black-box where the internal pathways of crustal genesis are unknown. The same source exergy is attributed to each co-product (there are several). Because co-products embody the same source exergy they shouldn't be added in a resource accounting analysis to avoid double counting the sources. The emergy of sedimentary (e.g. limestone, evaporites) and tectonic (e.g. granitic rocks, metamorphic rocks, etc.) rocks embody the same exergy (i.e. the GEB). Actually, approximately 10% of 2008 US metal/mineral emergy is double counted for this reason (Table 1).

Odum (1999, 2000b) estimated a linear relation between the specific emergy of lead (Pb) and its concentration. This relation results from topological emergy methodology (i.e. ore grade assumed to be directly, and linearly, related to environmental support of ore body creation). Topological emergy enrichment was extended to all crustal elements (Cohen et al., 2007) validated against economic relations with ore grade. Copper ore tonnage was negative $\log_{10}$ correlated with ore grade, a phenomenon consistent across crustal elements (Ibid.). Thus ore body specific emergy (for all crustal elements) was assumed linearly related with purity. This mass enrichment (ME; Ibid.) method is the most commonly applied method to compute the emergy of crustal materials (e.g. Rugani et al., 2011; Brown et al., 2009) but a thermodynamic link relating mass and exergy and thus specific emergy and transformity is still missing.

Every other resource in emergy accounting has both a transformity and specific emergy. This assertion is not readily evident because many resources are almost always expressed as either a transformity (e.g. sunlight, wind, fossil fuels, etc.) or specific emergy (e.g. metals, minerals, fertilizers, etc.). It's possible, though impractical, to express sunlight as mass or fertilizer as chemical exergy which makes possible the expression of their specific emergy or transformity respectively. All transformities are the ratio of a resource's emergy to its intrinsic exergy. It is the dissipation of exergy which carries materials along the energy hierarchy, where such materials are organized into material hierarchies (Odum, 1999). Thus exergy links the energy and material hierarchy, represented by transformity and specific emergy respectively. The general relationships are as follows:

$$\tau = {}^{\varepsilon}\!/_{\beta} \tag{1}$$

$$\varepsilon = \tau\beta \tag{2}$$

$$\beta = {}^{\varepsilon}\!/_{\tau} \tag{3}$$

Where, transformity, τ (seJ/J), is linked to specific emergy, ε (seJ/g), through specific exergy, β (J/g). A linear relation between specific emergy and transformity is possible only if specific exergy is a linear function. As shown later, specific exergy of minerals is a non-linear function of molecular purity.

Martinez et al. (2007) argued for the exergeocology method, as opposed to the emergy method, focussing on the chemical and concentration exergy of minerals (discussed later). They characterize mineral value with the combination of these two exergies along with mineral exergy replacement cost, which is the exergy required to remake the properties of a mineral deposit by means of human technology. Mineral exergy, in this way, is defined as the minimum energy required to remake a deposit from the reference environment (RE) via a reversible process. Crustal exergy can then be tallied along with other resource exergies (e.g. fossil fuels, water kinetic, etc.) in life-cycle-assessment as an exergy-based impact assessment method (Valero and Valero, 2012; DeWulf et al., 2008).

De Vilbiss (2013) utilized external energy needed to concentrate a mineral to characterize a 'transformity' enrichment factor. Methodologically, this approach had many flaws, discussed later, but it made possible the innovations of the current work. Jamali-Zghal et al. (2014) explored integrating exergoecology with emergy to underscore crustal specific emergies; however their analysis had several flaws. For example, the average transformity of the crust was determined to be the weighted average transformity of Earth's tripartite (Table 1, Ibid.). As shown later, average crust transformity (seJ/J) is the emergy of the crust divided by the exergy of the crust. Further, the analysis summed a mineral's exergy replacement cost with its intrinsic chemical and concentration exergies. Mineral exergy replacement cost is a measure of human investment needed to remake an ore deposit, which is far from optimum as evidenced by humanity's rapidly evolving technological efficiency. Exergy replacement cost is not a characteristic held by the mineral itself and therefore adding it with chemical and concentration exergy fallaciously inflates a mineral's potential to do work (i.e. its exergy).

Table 1
Most important metal and mineral emergy inputs in 2008 to the US economy (data from NEAD, 2014).

Item	Mass (2008 MT)	Specific emergy (seJ/g)	Emergy (2008 E ± 22 seJ)	% tot. (%)	Type	Mass enrichment or source[a]	Mean crustal abundance mg/kg	Mine crustal abundance mg/kg
Limestone	885203000	$9.50E+09$	841	83	Mineral	Limestone		
Dolomite	59400000	$9.50E+09$	56	6	Mineral	Limestone		
Iron ore	54000000	$5.78E+09$	31	3	Metal	3.4	56300	193780
Lead	423000	$4.80E+11$	20	2	Metal	285.7	14	4000
Phosphate rock	30900000	$6.45E+09$	20	2	Mineral	3.8	1050	3990
Copper	1310000	$9.80E+10$	13	1	Metal	58.3	60	3500
Gypsum	12700000	$9.50E+09$	12	1	Mineral	Limestone		
Zinc	778100	$7.20E+10$	6	1	Metal	42.9	70	3000
Molybdenum	61400	$7.00E+11$	4	0.4	Metal	416.7	1.2	500
Cadmium	745	$3.36E+13$	3	0.2	Mineral	20000.0	0.15	3000

[a] Mass enrichment means the ratio of mine grade to average crustal abundance.

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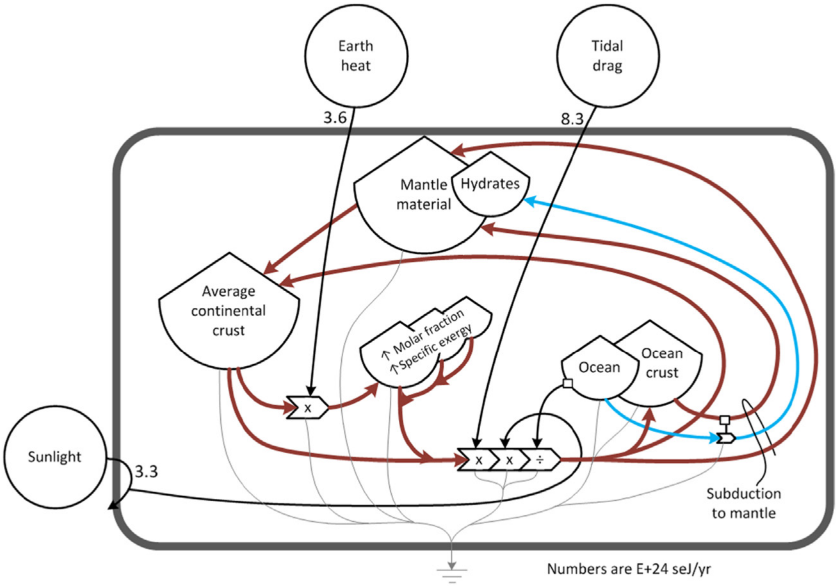

Fig. 1. Systems diagram of continental cycling, showing the GEB driving the mineral cycles of concentration and crustal accretion (numbers from Brown and Ulgiati, 2010).

2. Methods

2.1. Emergy of material inputs to US economy

Table 1 shows the major material inputs to the US economy in 2008 (see Sweeney et al., 2007 for explanation). Its emergy is dominated by limestone or items approximated to limestone's UEV. Note that average crustal specific emergy has changed due to updated values for the mass of the crust and its turnover time (see Section 2.2).

2.2. Average crustal specific emergy

The GEB drives, among many things, the cycling and concentration of crustal minerals. Crustal cycling is driven from below by the geothermal engine and from above by the solar and tidally driven erosive forces (Odum, 2001). In more recent geologic time biology has contributed to crustal erosion. The generation of crustal material involves emplacing new magma from the mantle. Gross crustal growth has always been about 3 km^3/yr but by circa 3 Ga recycling brought net growth to zero (Cawood et al., 2013). Probably this is when modern plate tectonics initiated subduction (i.e. crustal recycle).

Earth's crust embodies billions of years of the GEB. During this time the GEB is assumed constant because we don't understand completely Earth's geodynamic history (e.g., the rate of Earth's cooling; Dobretsov, 2010, or tidal friction due to varying ocean volume and continental exposure; Korenaga, 2013). Thus details of crustal genesis are not considered (Fig. 1). Also fossil fuel formation is excluded. Our model shows the modern general material flow from continents to the oceans via the effects of sunlight and tidally driven erosive forces. Subduction reassembles continents or separates the crust into the mantle. Ocean drains into the mantle mostly by hydrothermal circulation and some by subduction (Rea and Ruff, 1996).

To estimate the average steady-state specific emergy of the general crust mixture we only need the GEB (assumed constant) along with average replacement time (2.4–2.5 Ga; Taylor and McLennan, 1995; Veizer and Jansen, 1985) of the considered mass of the continental crust. Using the upper limit age, the emergy of the continental crust is the product of crustal age and the GEB (i.e. $2.5\,E+09$ yr × $15.2\,E+24$ seJ/yr = $3.80\,E+34$ seJ).

Earth is practically closed-to-matter and so its elemental endowment is fixed. Though the composition of lower crust is difficult to establish (Korenaga, 2013) we distinguish crust from the underlying mantle due to its phase and chemical enrichment of certain elements e.g. U, Th, and K (Huang et al., 2013). The mass of the continental crust is 2.171 E+25 g (Peterson and Depaolo, 2007). Average crustal specific emergy is thus the ratio of crustal emergy to crustal mass ($3.80\,E+34$ seJ/$2.171\,E+25$ g = $1.75\,E+09$ seJ/g).

2.3. Chemical exergy

Mineral chemical exergy expresses the minimum work required for chemically combining the reference substances dispersed in the RE (Szargut et al., 2005; Valero, 2008). The RE represents a "dead" planet whose chemistry has fully reacted, dispersed, and mixed. Its chemical composition is fixed by the natural environment (Valero, 2008). For each element the most abundant molecule, which also possesses a Gibb's formation energy within a 'stable' range, is classified as a reference substance. This is known as Szargut's *criterion of partial stability* (Szargut et al., 2005) and it generates some negative chemical exergies for many minerals more stable than reference substances (Table 2). This leads to skepticism about the chosen RE. However, this RE is preferable to others whose resulting dead planets don't resemble Earth (see discussion in Valero, 2008).

It's theoretically inconsistent in emergy to have a negative UEV. Zero is the smallest UEV, representing the quality of zero potential energy. Just as there is no sub-zero Kelvin, UEVs indicate quality on an absolute scale. Later we discuss how to utilize chemical exergies on both sides of zero for mineral transformities. But first, we must address the concept of an average chemical crustal transformity, as part of a logical sequence of possibilities which eventually deliver us to our final methods.

Chemical exergy b_{ch} for a mineral body is the sum of the standard chemical exergy $b_{ch,i}$ and mixing exergy $RT_0 \ln x_i$ for each constituent mineral i according to their molar fractions x, Eq. (4). Note the similarity of Eq. (4) to the Gibb's free energy Eq. (5). Gibb's

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Table 2
Selected minerals with negative chemical exergies (from Valero et al., 2012).

Commonly extracted minerals	Formula	Chemical exergy (J/g)	Average crustal abundance (parts per billion)
Colemanite	$Ca_2B_6O_{11}(H_2O)_5$	−1938	0.38
Orthoclase/K-feldspar	$KAlSi_3O_8$	−46	2676
Apatite	$Ca_5(PO_4)_3(OH)_{0.33}F_{0.33}Cl_{0.33}$	−46	5.02
Kaolinite	$Al_2Si_2O_5(OH)_4$	−35	206
Diaspore	$AlO(OH)$	−22	187
Hydragillite/Gibbsite	$Al(OH)_3$	−18	112

free energies, however, are negative for all crustal minerals (Valero et al., 2012).

$$b_{\text{ch,solution}} = \sum_{i=1}^{m} x_i \left(b_{\text{ch},i} + RT_0 \ \ln x_i \right) \tag{4}$$

$$\Delta G_{f,\text{solution}} = \sum_{i=1}^{m} x_i \left(\Delta G^0_{f,i} + RT_0 \ \ln x_i \right) \tag{5}$$

The emergy of the exergy of concentration (in a concentrated ore body) is discovered by first determining the average crustal transformity. The chemical exergy of the upper continental crust is the application of Eq. (4) to all crustal minerals, which is 366.56 kJ/mole or 2324 J/g crust (157.7 g/mole average crust). The average chemical transformity for upper continental crust is the ratio of average crustal specific emergy (1.75 E+09 seJ/g; Section 2.2) to average chemical exergy (2324 J/g) which is 7.53 E+05 seJ/J. However this assumes that mineral quality is equivalent across minerals. In other words, chemical exergy carries the same transformity for every mineral, be it calcite ($CaCO_3$) or cinnabar (HgS). The efficacy of this assumption is questionable.

2.4. Energy needed to concentrate and concentration exergy

Perhaps concentration is more relevant than chemical potential to underscore mineral quality. Faber (1984) and Faber et al. (1987) describe the minimum energy needed to separate a substance in an ideal mixture by assuming volumetric fraction equals molar fraction (i.e. that every kind of molecule occupies the same volume; Eq. (6)). $\beta_{i,c}$ is the external energy needed to concentrate, expressed in J/mole, where R is the gas constant, T is absolute temperature, and x is the molar fraction (mole/mole) of mineral i at concentration c. The energy needed to concentrate goes to zero at purity, and to infinity at low concentrations.

$$\beta_{i,c} = -RT \left[\ln x_{i,c} + \frac{\left(1 - x_{i,c}\right)}{x_{i,c}} \ln \left(1 - x_{i,c}\right) \right] \tag{6}$$

Later, several papers (Valero and Valero, 2012; Valero, 2008; Valero et al., 2008) use Eq. (6) to describe concentration exergy Eq. (7) which is the magnitude of energy needed to concentrate (to complete purity) from average abundance minus the magnitude of concentration energy from mine abundance (Fig. 2). Note the y-axis differs from previous authors who thought it to be in units of kJ/mole.

$$\begin{aligned} b_{i,c} &= \beta_{i,c} - \bar{\beta}_i \\ &= RT \left[\ln \frac{\bar{x}_i}{x_{i,c}} + \frac{\left(1 - x_{i,c}\right)}{x_{i,c}} \ln \left(1 - x_{i,c}\right) - \frac{\left(1 - \bar{x}_i\right)}{\bar{x}_i} \ln \left(1 - \bar{x}_i\right) \right] \end{aligned} \tag{7}$$

There are theoretical issues surrounding the use of concentration *exergy* to compute UEVs. For instance, exergoecology (Valero et al., 2008) combines the exergy of chemical and concentration potential to characterize the natural capital of minerals. However, concentration is already accounted in the mixing term for chemical exergy (see Eq. (4)). Concentration *exergy* references only mineral abundance, and is therefore the same for any mineral whose concentration parameters are identical to another mineral (i.e. concentration exergy is not unique to any particular mineral, unlike chemical exergy or Gibb's formation energy). Further, a mineral can have negative concentration exergy if its concentration is below average, but we cannot have a negative transformity. The amount of material below average concentrations equals the amount above average concentrations. Thus, globally, the continuous flux of crust produces essentially no net concentration exergy. Therefore it's impossible to have a global transformity for crustal concentration exergy.

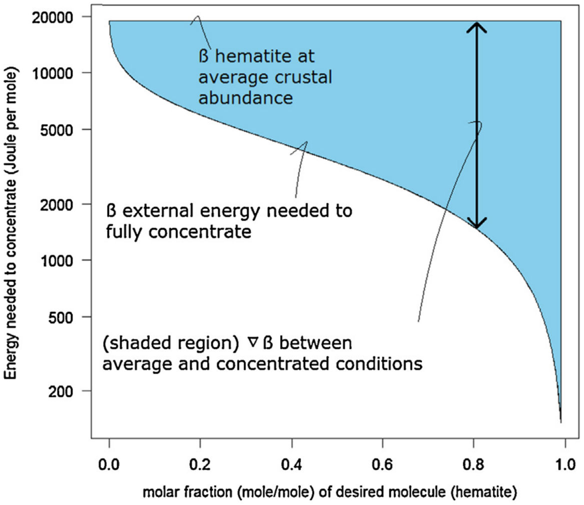

Fig. 2. (Top-horizontal line) energy needed to concentrate to purity from average crustal abundance, (bottom curve) concentration energy with variable concentration, and the difference (shaded region) which represents the potential (concentration exergy) for the mineral hematite.

Due to these issues De Vilbiss (2013) used concentration *energy* Eq. (6) rather than concentration *exergy* Eq. (7) to link crustal mass quality with energy quality. The energy needed to concentrate (different from concentration exergy) was useful because the resulting curve is continuous from zero abundance (infinity energy needed to concentrate) through to purity (zero energy needed to concentrate). The smaller the energy needed to concentrate, the higher its inverse, thereby quantitatively indicating a more concentrated substance to have higher quality. The ratio of the energy needed to concentrate at average abundance to that at the mine abundance indicated an enrichment factor from which specific emergies were calculated.

This method was not desirable except in the absence of any other thermodynamic method in the literature to link crustal specific emergy with its transformity. It was considered an improvement,

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Table 3
Unique mineral chemical and Gibb's transformities for the 10 most important minerals for the US economy[1].

Item	Mineral i	Mine abundance (mg/kg)[2]	Molar mass (g/mol)	Average molar fraction, $\bar{x}_i$	Mine molar fraction, $x_{i,\mathrm{mine}}$	Mixing exergy (kJ/mole)	$\bar{\tau}_{\Delta G,i}$ (seJ/J)	$\bar{\tau}_{ch,i}$ (seJ/J)
Limestone	Calcite	950000	100.09	1.26E-02	9.68E-01	11	3.09E+07	2.19E+09
Dolomite	Dolomite	950000	184.4	1.20E-03	9.42E-01	17	8.74E+06	4.86E+08
Iron ore	Taconite	193780	215.6	2.87E-05	1.50E-01	21	7.70E+05	9.30E+06
Lead	Galena	4000	239.3	4.40E-06	2.64E-03	16	1.17E+08	1.18E+06
Phosphate rock	Phosphate rock	3990	310.2	1.42E-03	2.05E-03	1	2.91E+06	6.76E+07
Copper	Chalcopyrite	3500	183.5	5.71E-05	3.01E-03	10	8.78E+07	4.29E+05
Gypsum	Gypsum	950000	762.1	1.26E-04	7.97E-01	22	2.54E+06	4.73E+08
Zinc	Sphalerite	3000	97.5	1.61E-04	4.85E-03	8	1.62E+08	4.74E+05
Molybdenum	Molybdenite	500	160.1	1.80E-06	4.93E-04	14	7.47E+07	3.42E+05
Cadmium	Greenockite	3000	144.5	1.26E-07	3.27E-03	25	1.25E+08	7.22E+05

[1] Data from Valero et al. (2012) except for [2] from NEAD (2012).

but suffered from theoretical issues itself. For example, the energy needed for concentration is not exergy and therefore a transformity, strictly speaking, cannot be yielded from the ratio of emergy to concentration energy. The link between transformity and specific emergy was still missing.

2.5. Adding concentration exergy with chemical exergy

We question the validity of adding concentration exergy with chemical exergy. To add chemical and concentration exergies (in the emergy method) implies they are the same kind of resource requiring the same environmental support (i.e. they have the same quality). The reference datum differs between these two kinds of exergy. Though similar, concentration exergy is the gradient of a molecule's abundance relative to its average abundance in the crustal soup, whereas chemical exergy results from the deviation of *chemical composition* of the material from the (aggregate) composition of the commonly appearing components of the RE (Szargut, 1989). Different reference frames connote different kinds of exergy, which, in the emergy method, may be added only after conversion to a common unit (seJ). However, we don't yet know how to partition Earth's environmental support among the genesis of chemical exergy and concentration exergy of mineral bodies.

According to Eq. (7) minerals below average crustal abundance have negative concentration exergy. From this initial condition the concentration process would be endothermic, and thus doesn't drive work. Negative, in this case, depends on the reference datum. If we consider only minerals above their average crustal abundance, chemical exergy still out measures concentration exergy except for minerals with very small chemical exergies that are also highly concentrated.

For example Colemanite and Orthoclase/K-feldspar (Table 2) have chemical exergies more negative than any amount of possible concentration exergy can negate (even in a pure deposit). Therefore negative exergy for these minerals are unavoidable. Keep in mind that negative chemical exergy results from the 'choice' of reference substances (Szargut, 1989).

Concentration exergy characterizes the heat generated upon molecular dispersal. Chemical exergy, on the other hand, characterizes the heat of sub-molecular (electron) chemical equilibration. Adding chemical and concentration exergies is analogous to summing thermal and kinetic exergies. While technically thermal and kinetic exergy both are a function of velocity (thermal being molecular scale velocity and kinetic being macro-molecular velocity), the energy of a wind gust accomplishes different work (in the geobiosphere) than an equal measure of atmospheric thermal gradient. The emergy method supposes the exergy of wind and temperature are additive only after being expressed in a form of energy common to both their geneses (e.g. sunlight). With regard to concentration and chemical exergy, it appears methodologically inconsistent, in the emergy method, to sum them because they refer to different kinds of potentials.

3. Results

3.1. Unique mineral transformities

Before continuing, note we reject two concepts; (1) a crustal average chemical transformity because it ignores any unique quality of mineral species, (2) summing chemical and concentration exergy because they reference different datum (see Section 2.5). Next we consider that each mineral has a *unique* chemical transformity, which is the ratio of average crust specific emergy $\bar{\varepsilon}$ by the absolute value (because we can't make use of negative transformities) of a mineral's chemical exergy at its average crustal abundance as follows:

$$\bar{\tau}_{\mathrm{ch},i} = \bar{\varepsilon}/|\bar{b}_{\mathrm{ch},i}| \tag{8}$$

Unique Gibb's transformities are found in similar manor as follows:

$$\bar{\tau}_{\Delta G,i} = \frac{\bar{\varepsilon}}{|\Delta\bar{G}_i|} \tag{9}$$

Mixing exergy (not to be confused with concentration exergy) refers to the difference in chemical exergy (or Gibb's energy) between mine and average crustal conditions (e.g. $\Delta G_{\mathrm{min}\,e,i} - \Delta\bar{G}_i = RT\ln\frac{x_{i,\mathrm{min}\,e}}{\bar{x}_i}$). The Gibb's and chemical transformities for the 10 highest emergy contributors to US economic metabolism range four orders of magnitude (Table 3).

3.2. Mixing exergy transformities

Next we account only the product of mixing exergy with a mineral's transformity. That is we assume the GEB is embodied in mineral concentrations (above average), but not in mineral formation. This assumption correlates with how rain is accounted in the emergy method i.e. the emergy of water increases with concentration and is zero at ocean purity (e.g. Watanabe and Ortega, 2011).

This assumption comes from acknowledging that the tripartite is not responsible for Earth's element endowment, which would affect mineral abundance and thus all exergy parameters.

Note Gibb's Eq. (5) and chemical exergy Eq. (4) have identical mixing exergy terms. Their transformities, however, depend on each mineral's standard free energy/chemical exergy, average crustal abundance, and molecular mass, all of which vary. There is no correlation between average crustal abundance and Gibb's or chemical transformities; nor is there relation between Gibb's and chemical transformities (Fig. 3).

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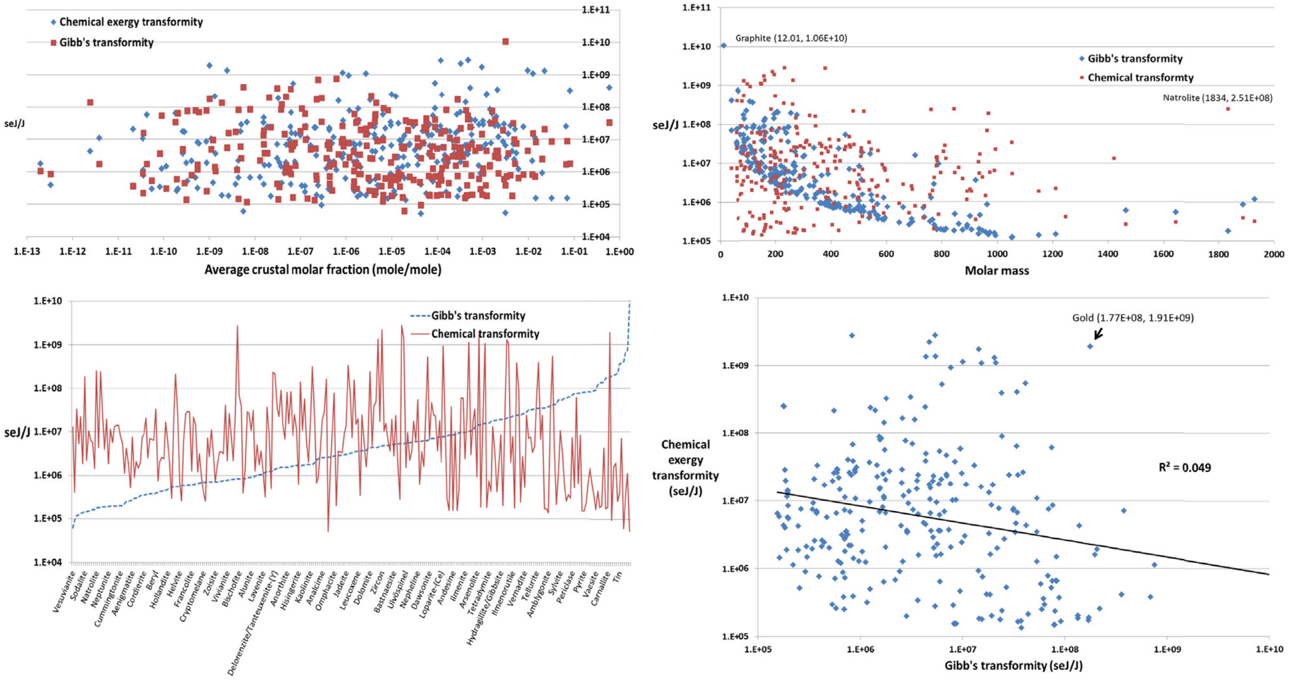

Fig. 3. Compilations for the 281 crust minerals for which Gibb's formation energy and chemical exergies are found (data from Valero et al., 2012). (top-left) No correlation between average crustal abundance and transformity; (top-right) transformity plotted against molecular mass reveals a curve for Gibb's transformities; (bottom-left) minerals plotted against transformity with ascending Gibb's transformities, the highest of which is Graphite's; (bottom-right) a very weak power-law association between Gibb's and chemical exergy transformities of the minerals.

Table 4
Specific emergies (seJ/g) of important mineral inputs to the 2008 US economy when applying two different transformities (Gibb's and chemical exergy) with two accounting procedures (total energy or mixing exergy only).

Item	$E \pm 09$ seJ/g using ME method	$E \pm 09$ seJ/g using $\tau_{\Delta G}$		$E \pm 09$ seJ/g using τ_{ch}	
	NEAD updated[1]	Total J[2]	Mixing J[3]	Total J[4]	Mixing J[3]
Limestone	9.8	17.3	0.2	118.9	117.2
Dolomite	9.8	9.4	0.1	23.4	21.6
Iron ore	6.0	8.2	0.2	27.1	24.7
Lead	497	6.5	0.9	1.8	0.039
Phosphate rock	6.7	5.6	0.0013	1.8	0.10
Copper, mine	101	9.1	0.4	1.8	0.011
Gypsum	9.8	2.3	0.027	5.0	6.7
Zinc	75	17.3	0.7	1.8	0.020
Molybdenum	725	10.5	0.5	1.8	0.015
Cadmium	34793	10.6	1.6	1.8	0.1

[1] NEAD (2012) specific emergies are updated to the new average crustal specific emergy (1.75E+09 seJ/g).
[2] Accounts total Gibb's energy of mineral including mixing term.
[3] Accounts only the mixing exergy.
[4] Accounts total chemical exergy including mixing exergy.

Minerals destroyed in human processing contribute all their chemical exergy (and emergy) to the economy. This material returns to the crustal cycle in short geologic time where minerals are reformed. Thus, ultimately only concentration was lost. Given in Table 4 are several specific emergies for ten prominent mineral/metal inputs to the USA economy in 2008 (as listed in the NEAD, 2012). The first column displays NEAD UEVs, which utilize the ME method. In the next four columns UEVs were calculated using the Gibbs and chemical exergy formulations, paired with two accounting procedures (total exergy and mixing exergy only).

Using chemical exergy transformity, and accounting all of limestone's chemical exergy, its specific emergy is more than an order of magnitude larger than when computed with the ME method. This indicates that this approach may not be justified as it would result in limestone's emergy dwarfing all other mineral, metal, fossil fuel, and renewable emergy contributions to the economy. Accounting only mineral mixing exergy with limestone's chemical exergy transformity results in a slightly smaller UEV. Accounting all of limestone's free energy using its Gibb's transformity yields around a one-order smaller UEV compared with using the chemical exergy transformity. The smallest limestone specific emergy is found by accounting only calcite's mixing exergy with its Gibb's transformity (Table 4).

4. Discussion: US mineral/metals emergy

To explore the efficacy of these new methods for computing the emergy of minerals, we examined their effect on the emergy driving the 2008 US economy as derived from the NEAD (2012). The NEAD makes use of the mass enrichment (ME) method (Sweeney et al., 2007; Cohen et al., 2007) to compute material UEVs. Concentrated non-renewables were 54% of total US emergy use in 2008 (Fig. 4a), of which minerals and metals represented 52% (Fig. 4b); thus 26%

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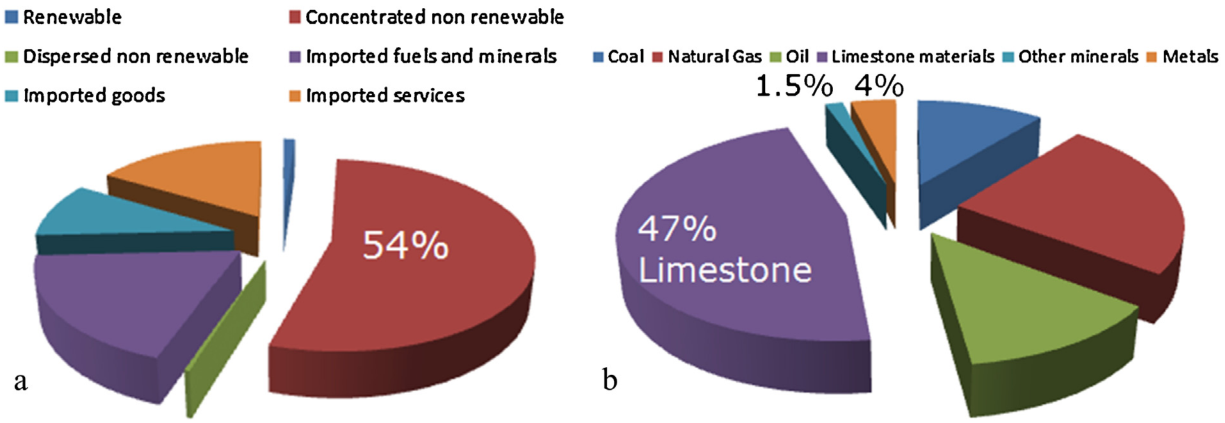

Fig. 4. Emergy contributions to the US economy from (a) all resources; (b) breakdown of concentrated non-renewables (data from NEAD).

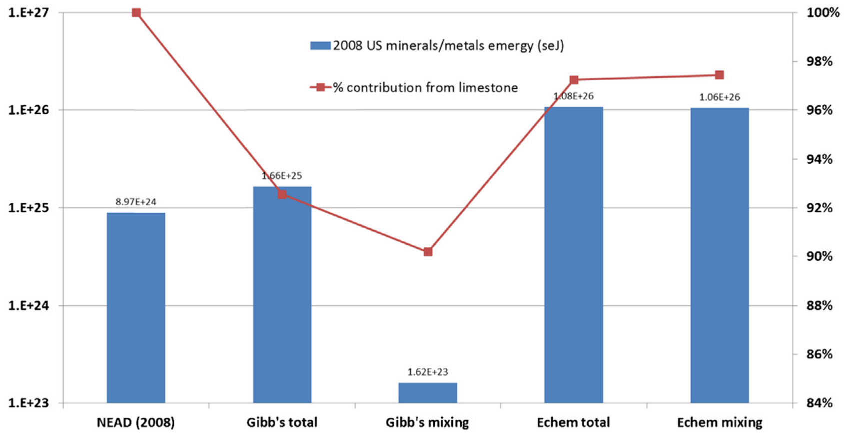

Fig. 5. Total emergy of minerals/metals supporting the 2008 US economy (left-axis) and percent contribution from limestone (right-axis). Different accounting procedures (described in 4) compose the *x*-axis. Note that the original NEAD accounting summed limestone with other crustal products, which were co-products that should not be summed; only the largest should be accounted.

of the total US emergy support is from minerals/metals, most of which is limestone.

Limestone (calcite) is the largest mineral contributor to the US economy (Table 1), and so may be the most important to consider when gauging the efficacy of our proposed methods. Originally 90% of US mineral/metal emergy came from limestone (Table 1). However, in this the limestone UEV is a co-product of the crustal cycle (Table 1; Odum, 2000a). Limestone emergy shouldn't be added with the other 10% of the mineral/metal emergy to avoid double counting the emergy sourced to the crust. Correcting this double-accouting requires 'ignoring' the other 10% according to emergy algebra rules (Brown and Herendeen, 1996). This correction is applied for comparison purposes (Fig. 5), and results in limestone emergy representing 100% of the US mineral/metal emergy (note, this method predates the current paper). In the four proposed methods all minerals are splits and can be summed. In these, limestone represents between 90.2 and 97.5% of the total minerals/metals emergy.

The NEAD US mineral/metal emergy is 8.97 $E+24$ seJ (Fig. 5). Compared with this value, the US mineral/metal emergy found by accounting *total* mineral chemical exergy yields the largest national emergy, 1.08 $E+26$ seJ/yr, a 1,106% increase. Accounting only mixing exergy with Gibb's mineral transformities yields the smallest national minerals/metals emergy 1.62 $E+23$ seJ/yr, a 98% decrease.

5. Conclusions

Open systems survive on inputs of potential energy (exergy). But equal measures of different forms of exergy may yield different effects. To correct for the different effects of different forms of exergy, Odum (1996) introduced a method of environmental accounting called emergy. In the emergy method, transformities express exergy quality from the donor-perspective. That is, a transformity reflects the environmental energy previously invested in yielding a presently available exergy.

Mass is more convenient to account crustal minerals, thus specific emergy was defined to be the product of transformity and exergy density (J/g). In this way "mass quality" is characterized as the environmental effort in producing available potential energy in mass form. To date, only one attempt has been made to link specific emergy and transformity for crustal minerals of varying purity (Jamali-Zghal et al., 2014). The work here builds upon this initial effort. For example rather than assuming the transformity of crust is the weighted average transformity of Earth's exergy sources (Ibid.), here it has been shown that minerals can be considered to possess unique transformities based on either their Gibb's formation energy or chemical exergies. This is an important contribution because without exergy, there is not emergy, and without emergy there is no transformity or specific emergy. Therefore specific emergy and transformity are linked through specific exergy.

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We dispel summing chemical and concentration exergies due to different reference datum (similar to the difference between thermal and kinetic energy potentials). Then we discuss the use of chemical exergies which fall on either side of zero for calculating mineral transformities (i.e. transformities exist on an absolute scale). The negative chemical exergies make questionable the chosen reference environment which produced them. Gibb's formation energies however do not depend on a chosen chemical reference environment. Thus we recommend using Gibb's mineral transformities.

One issue is whether to account the total exergy (or Gibb's formation energy) of a molecule or only the exergy associated with heightened concentration (known as mixing exergy). The implications of four proposed methods, (1) Gibb's transformity, (2) chemical exergy transformity, (3) accounting total exergy, and (4) accounting only mixing exergy, were applied to the minerals/metals supporting the 2008 US economy. Compared with the original estimates, accounting the entirety of mineral chemical exergy yields the highest national minerals/metals emergy (a 1,100% increase). Accounting only the Gibb's mixing exergy yields the smallest national minerals/metals emergy (a 98% decrease).

Note that accounting only the Gibb's mixing exergy is consistent with the emergy method for accounting the emergy of the chemical potential energy of precipitation (Odum, 1996). Also, accounting Gibb's mixing exergy leads to higher specific emergies for the more rare elements (e.g. Ca, Pb) and lower specific emergies for more common minerals (e.g. dolomite, gypsum). For these two reasons accounting only mixing exergy with Gibb's mineral transformities is the preferred mineral accounting procedure (among the options presented in this paper). This assertion, however, requires further examination.

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