Appendix 1: a modified strain energy model

I consider the elastic strain energy model to calculate the energy change associated with the replacement of an ion in a crystal with another one with different size. In the elastic strain energy model, all materials involved are considered to be elastic media. Accordingly, both the matrix and the trace element are treated as elastic media. Treating a trace element as an elastic medium is a gross simplification. However, by assigning a bulk modulus to the trace element, it is possible to evaluate the influence of "stiffness" of a trace element on the strain energy.

When a crystal is treated as an isotropic elastic medium, the displacement in the matrix and the spherical inclusion is given by (e.g., (Flynn, 1972)),

$$\vec{u}_{0,1} = \left(\frac{A_{0,1}}{r^3} + B_{0,1} \right) \vec{r} \tag{A-1}$$

where suffix 0 refers to those for the matrix and 1 to the trace element, and $A_{0,1}$ and $B_{0,1}$ are constants that are to be determined by the boundary conditions. The equation (A-1) has 4 unknowns, $A_{0,1}$ and $B_{0,1}$. The boundary conditions are: (1) $\sigma_{rr}(R) = 0$ (R is the radius the crystal (homogeneous stress caused by pressure is subtracted)), (2) σ_{rr} and u are continuous at the boundary between 1 and 0 ($r = \tilde{r} \equiv (1 + \varepsilon) r_0$). Note that the displacement of the boundary, i.e., ε, is also an unknown that must be determined by solving the force balance and displacement continuity equations.

The solution to (A-1) is somewhat tricky to obtain because of the effects of the image force, i.e., the condition $\sigma_{rr}(R) = 0$ (Eshelby, 1951, 1954). We consider first a finite crystal with a finite radius R and consider the proper boundary conditions including the ones at the surface ($r=R$). Then we let $R \to \infty$. The condition of zero (excess) normal stress at $r=R$ leads to

$$B_0 = \frac{4G_0}{3K_0} \frac{A_0}{R^3}. \tag{A-2}$$

Note that although B_0 becomes vanishingly small at $R \to \infty$, it leads to a *finite* volume change of a crystal due to the effect of the image force (Eshelby, 1951, 1954). The volume change of a crystal due to this displacement is

$$\Delta v_c = 4\pi R^2 u(R) = 4\pi A_0 \frac{K_o + \frac{4}{3}G_o}{K_o} = 12\pi A_0 \frac{(1-v_0)}{1+v_0}. \tag{A-3}$$

In addition, there is an explicit volume change caused by the addition of a trace element. Adding the volume change by replacing one atom (ion) with another, the net change in the volume of the whole system is given by

$$\Delta v = \Delta v_c + (v_1 - v_0) = 12\pi A_0 \frac{(1-v_0)}{1+v_0} + (v_1 - v_0) \tag{A-4}$$

where v_1 are the volume of mineral after the trace element is dissolved and v_0 is the volume of the mineral before the trace element dissolution (the volume

difference $(v_1 - v_0)$ may correspond to the volume change associated with the formation of point defects). The normal stress at the boundary $(r = \tilde{r} \equiv (1+\varepsilon) r_0)$ from the inclusion comes from the initial pressure + displacement. The conditions of continuity of stress and displacement lead to

$$-\frac{4 G_0 A_0}{\tilde{r}^3} + 3 K_0 B_0 = 3 K_1 \left(1 - \frac{r_1}{\tilde{r}}\right) \tag{A-5a}$$

$$\frac{A_0}{\tilde{r}^2} + B_0 \tilde{r} = B_1 \tilde{r} = \tilde{r} - r_0 \tag{A-5b}$$

where $K_{0,1}$ are the bulk moduli of the host crystal and the trace element respectively.

From (A-5b), $B_1 \tilde{r} = \tilde{r} - r_0 = B_1 r_0 (1+\varepsilon) = r_0 \varepsilon$, so that $B_1 = \frac{\varepsilon}{1+\varepsilon}$. Using (A-2) and taking the limit of $R \to \infty$, one obtains $A_0 = \varepsilon (1+\varepsilon)^2 r_0^3$.

Therefore the coefficients in equation (A-1) are given by,

$$A_0 = \varepsilon (1+\varepsilon)^2 r_0^3 \tag{A-6a}$$

$$A_1 = 0 \tag{A-6b}$$

$$B_0 = \varepsilon (1+\varepsilon)^2 \frac{4 G_0}{3 K_0} \left(\frac{r_0}{R}\right)^3 \tag{A-6c}$$

$$B_1 = \frac{\varepsilon}{1+\varepsilon}. \tag{A-6d}$$

Inserting these relations into (A-5a) and ignoring the terms containing $\frac{r_0^3}{R^3}$, one

obtains

$$\varepsilon = \beta\left(\frac{r_1}{r_0} - 1\right) \tag{A-7}$$

with $\beta \equiv \frac{K_1}{K_1 + \frac{4}{3}G_o}$. Therefore for a very stiff trace element ($K_1 \gg G_0$), $\varepsilon \approx \frac{r_1}{r_0} - 1$ and $\tilde{r} \approx r_1$

whereas for a very soft trace element (e.g., noble gas elements), $K_1/G_o \ll 1$, so

$\varepsilon \approx 0$ and $\tilde{r} \approx r_0$.

The enthalpy associated with the incorporation of trace element is given by

$$\Delta h^{ela} = \Delta u^{ela} + P\Delta v \tag{A-8}$$

where Δu^{ela} is the strain energy and Δv is the volume change of a crystal due to

the incorporation of a trace element. From (A-4) and (A-6a), the volume change is

given by

$$\Delta v = 4\pi r_o^3\left(\frac{r_1}{r_0} - 1\right)\left[1 + \frac{K_o}{K_o + \frac{4}{3}G_o}\left(\frac{r_1}{r_0} - 1\right)\right]^2 + \frac{4\pi}{3}r_0^3\left(\frac{r_1^3}{r_0^3} - 1\right). \tag{A-9}$$

The volume change due to this process is a fraction of atomic volume and is small

compared to the volume change associated with vacancy formation.

The strain energy can be calculated as

$$\Delta u^{ela} = 4\pi \left[\int_0^{\tilde{r}} w_1(r) r^2 dr + \lim_{R \to \infty} \int_{\tilde{r}}^R w_0(r) r^2 dr \right] \qquad \text{(A-10)}$$

where

$$w_{0,1} = \frac{\lambda_{0,1}}{2} \left(\frac{du_r^{0,1}}{dr} + 2 \frac{u_r^{0,1}}{r} \right)^2 + \mu_{0,1} \left[\left(\frac{du_r^{0,1}}{dr} \right)^2 + 2 \left(\frac{u_r^{0,1}}{r} \right)^2 \right] \qquad \text{(A-11)}$$

are the strain energy densities in the host crystal (0) and in the trace element (1) respectively and where $\lambda_{0,1}, \mu_{0,1}$ are the Lamé constants of the matrix ("0") and the trace element ("1").

From (A-5), (A-6), (A-7) and (A-11), one gets,

$$w_0 = \frac{9}{2} K_0 B_0^2 + \frac{6 G_0 A_0^2}{r^6} = 2 A_o^2 \mu_o \left[\frac{4 G_o}{K_o} \frac{1}{R^6} + \frac{3}{r^6} \right] \qquad \text{(A-12a)}$$

$$w_1 = \frac{9}{2} K_1 B_1^2. \qquad \text{(A-12b)}$$

Inserting equations (A-6) and with (A-10),

$$\Delta u^{ela} = 6\pi r_0^3 \varepsilon^2 (1+\varepsilon) \left(K_1 + \frac{4}{3} G_0 \right)$$
$$= 6\pi \frac{K_1^2}{K_1 + \frac{4}{3} G_0} r_0^3 \left(\frac{r_1}{r_0} - 1 \right)^2 \left[1 + \frac{K_1}{K_1 + \frac{4}{3} G_0} \left(\frac{r_1}{r_0} - 1 \right) \right]. \qquad \text{(A-13)}$$

The equations (A-8), (A-9) and (A-13) give the change in the elastic enthalpy, Δh^{ela}, upon the dissolution of a trace element.

Appendix 2: Electrostatic charge and effective elastic constants

Strain energy model is formulated in terms of the size of the site (r_o), the size of a trace element (r_I) and elastic constants of relevant materials (trace element and the host crystal). Comparing a theoretical relationship such as the equations (T-1) through (T-3) with the observed data on element partitioning, one can calculate the effective elastic constant. However, when one does such an exercize, the size of the site at which a peak of partition coefficient is supposedly located does not always agree with the ionic radius of the host ion (e.g., (Blundy and Dalton, 2000)). For instance, in the case of the M2 site of clinopyroxene where trace elements with 3+, 2+ and 1+ charge could go, the estimated r_o from the Onuma diagram agrees well with the ionic radius of the host ion only for trace elements with 2+ charge. The inferred r_o is substantially larger than the ionic radius of the host ion for trace elements with 1+ charge, and it is less than the ionic radius for trace elements with 3+ charge.

This can be attributed to the influence of the charge on the atomic displacement near a point defect. When a point defect such as a vacancy is formed in an ionic crystal, it will create elastic and electric singularities. When a trace element is inserted into that site with an electric charge different from the host ion, it will generate electrostatic force to cause displacement of the ions surrounding it. For a trace element with a charge less (more) than that of the host, the force is repulsive (attractive) and the size of the site will increase (decrease). This explains the systematic shift of r_o with the charge of the trace element.

This effect is largest when the trace element is neutral, i.e., the noble gases.

Appendix 3: Some notes on the estimation of $(EEC)_{obs}$

When the solubility of trace elements in a mineral is measured (e.g., the noble gas solubility in bridgmanite (Shcheka and Keppler, 2012)), the elastic strain energy model can be directly compared with the data on the element solubility to calculate the effective elastic constant, EEC. In most of trace elements, the available data are the partition coefficients rather than the solubility. In these cases, we need to make an assumption that the concentration of these elements in the melts is independent of the properties of the element. If this assumption is valid, then one can translate the partition coefficient as the solubility, and then compare the results with a model of element solubility (elastic strain energy model)[1].

There is another complication in estimating the EEC. When the EEC is calculated from the partition coefficients or the solubility, various data for a range of ionic radius (or atomic radius), r_I, are used. This is not trivial because the EEC itself likely depends on the size of host ion (r_o) and the size of the trace element (r_I), but the relationship between these parameters and the EEC is unknown. Furthermore, even the size of the site, r_o, estimated from the Onuma diagram is sometimes different from the value expected from the ionic radius of the host ion and is treated as an unknown parameter to be determined from the experimental observations (e.g., (Blundy and Dalton, 2000)). Under these circumstances, it is justifiable to obtain a rough estimate of the EEC first assuming that it is independent of r_o and r_I, and explore the correlation of the effective elastic constant with other parameters such as r_o and r_I because the dependence of the EEC on these parameters is weak in comparison to the variation in the

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[1] This assumption is not valid for the noble gases.

EEC. This can be seen as follows. The bulk modulus of polyhedron depends on the ionic

size as $K_{i,o} \propto Z_{i,o} / \left(r_{i,o} + r_{oxy} \right)^{4}$ (corrected from (Hazen and Finger, 1979)) where r_{oxy} is the

radius of oxygen ion and $Z_{i,o}$ is the electric charge of the trace element or the host ion.

When $r_{i,o}$ changes from 0.10 to 0.14 nm, $K_{i,o}$ changes ~30% that is small compared to a

variation of the *EEC* among different sites (a factor of ~10-100; (Blundy and Wood,

2003)). Therefore such a procedure of estimating the effective elastic constant can be

justified as a first-order approximation.