Usage Report for Fiscal Year 2017

Project Title: Prediction of Crystal Structure and Properties

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1. Background and purpose of the project, relationship of the project with other projects

Growing from a series of collisions of planetesimals and planetary embryos, the loss of volatile elements and core formation shaped the compositional evolution of Earth. Volatile elements in the bulk silicate earth are depleted relative to CI chondrites, most primitive stony meteorites belonging to the carbonaceous chondrites with chemical compositions similar to the Sun's photosphere, and believed to represent the average nebula composition in proportion to their volatility. A general trend exists that the relative abundance of volatile elements in the silicate earth should decrease with increasing volatility. However, concentrations of many elements such as the lithophiles Au, Cu ,Ag and halogens (Cl, Br and I) fall below this trend. Typical examples are siderophile and chalcophile Au, Cu, Ag, *etc.* that are often suggested to be extracted into the Earth's core. Recently, several new prospective have been proposed to explain the depletion mechanism of some of the Earth's volatile elements that helped to clarify the understanding of the Earth's accretion and to constrain the compositional materials when Earth accreted.

The heavy halogens Cl, Br, and I were found to deplete by an order of magnitude more than would be predicted on the basis of their assumed volatility. This anomaly might have played a key role in the evolution of life on Earth by affecting the ocean salinity, because most of these heavy halogens (80%-90%) reside in Earth's surface reservoirs. Several explanations have been put forward to address this intriguing problem. In a very recent work, halogen contents in all chondrite groups were estimated, by considering contamination in the meteorites studied and using high-sensitivity neutron-irradiation noble gas mass spectrometry, to be much lower that indicating a higher CI-chondrite normalized halogen abundance than previously reported and usually accepted values. Combining with the argument that Cl may have a lower condensation temperature, the authors in the work pointed out that heavy halogens in the bulk silicate earth are not depleted relative to elements that have similar volatility. Even so, a volatile loss is needed to meet the requirement of present-day Earth's halogen concentration level. The depletion mechanism of volatile elements is complicated. The formation of Earth, a very complex process expected to be determined by the way how the volatiles were lost but the details are still not fully understood. The current abundance and distribution of volatile elements in the bulk silicate earth is a manifestation of the role the volatiles played in Earth's chemical evolution. The understanding of the depletion mechanism is critical to the construction of an Earth's accretion model in order to resolve many fundamental geological problems. In the case of heavy halogens, the depletion may be a result of several effects, such as Moon-forming giant impact, partial melting and evaporation of rock caused by planetesimals during accretion and possibly partial sequestration into Earth's core. The Earth's core is expected to contain around 85 wt% Fe and 5 wt% Ni alloyed with 10 wt% of minor lighter components (possibly S, Si, O, C, H, etc.). Numerous research has been performed to address the enigma of the iron-light element systems at the core pressure. The relative concentrations of the volatile elements, although with some exceptions, are believed to be related to the oxygen fugacity. Iron with its multiple oxidation states in the Earth's minerals controls the oxygen fugacity and oxygen budget. The recent experimental synthesis of a novel FeO_2 near the lower mantle pressure with an apparently high iron oxidation state may also affect the distribution of the volatiles. Many First principles calculations and structure predictions have been used to search for possible structures of iron compounds at the Earth's core pressure in an effort to better understand the structures and structural transformations that may help to interpret Earth's core formation and the observed seismic anisotropy as well as to constrain the concentration of light elements in the core. However, to our best knowledge, no investigations of iron halides at Earth's core conditions has been performed. In this contribution, we report results on the search of potential stable crystalline phases of iron halides at 25, 70, 135 and 360 GPa relevant to the pressures at the Earth's outer and inner mantle and core, respectively.

2. Specific usage status of the system and calculation method

During the fiscal year 2017, we have used about 80% of the total allocated CPU hours and, the rest 10% will be used up at the end of this financial year. We searched for FeXn (X=Cl, Br and I, n =1/4, 1/3,1/2, 1, 2, 3, 4) ground-state structures through CALYPSO methodology as implemented in CALYPSO code. Our structure searches with system sizes that ranging from 2 to 4 formula units per simulation cell were performed at pressures of 25, 70, 135 and 360 GPa. The total energy calculations and local structural relaxations were carried out using the density functional theory as implemented in the VASP code. To deal with the effects of changing temperature on the Helmholtz free energy, we incorporated the effects of thermal vibrations (phonons) using PHONOPY code.

3. Result

At ambient pressure, $FeCl_3$, $FeBr_3$, $FeCl_2$, $FeBr_2$ and FeI_2 are found to be stable with the respective experimentally observed structures. All these crystals consist of layers of edge-sharing octahedra with Fe located at the centers and linked through the halogens forming the edges. Both $FeCl_3$ and $FeBr_3$ have BiI_3-type structure ($R\bar{3}$ space group). In these structures, six octahedrals in each layer create a octahedral-shaped void and the Fe atoms occupy a hexagonal closest-packing sublattice. The crystal structures of $FeCl_2$ and $FeBr_2$ can be interpreted as the insertion of additional Fe atoms into the voids of corresponding $FeCl_3$ and $FeBr_3$ frameworks forming the $CdCl_2$-type structure ($R\bar{3}m$ space group) and CdI_2-type structure ($P\bar{3}m1$ space group), respectively. FeI_2 has the same crystal symmetry as $FeBr_2$.

Structure prediction calculations were performed on several stoichiometric FeX_n (X=Cl, Br and I, n =1/4, 1/3,1/2, 1, 2, 3, 4) at 25 GPa, 70 GPa, 135 GPa and 360 GPa. Here we only discuss the most stable phases obtained at the pressures considered (the stability of the newly predicted phases will be discussed below) and the dynamical stability of these stable phases were verified with the calculation of the phonon dispersions. At high pressures, $FeCl_2$, $FeBr_2$ and FeI_2 was predicted to exist in $Pa\bar{3}$ symmetry, while $FeCl_3$ and $FeBr_3$ adopt the $R\bar{3}c$ space group. Similar to the structures at ambient pressure, the crystals are built from octahedron blocks, suggesting similar Fe-halogen bonding environment. However, the linkage between these building blocks changes from edging-sharing to vertex-sharing. The structural transformation is not unlike that of the packing of the oxygen atoms in high pressure crystalline silica. In cubic FeX_2, Fe atoms occupy the face-centered cubic sites. FeI_3, which does not exist at ambient pressure start to be become stable at 25 GPa and has *R*32 symmetry. In this structure, two octahedra fused through face-sharing to form a larger building unit. The fundamental units are connected via vertices' sharing.

Only $FeCl_2$ and FeI_2 have been studied at high pressure by experiment. At 0.6 GPa, $FeCl_2$ transforms from the $CdCl_2$- to the CdI_2-type structure and remains stable at pressure up to 65 GPa. The calculations reproduced the phase transform at 0.15 GPa, which is in good agreement with the experiment. However, in contrast to the experimental observation, calculations show CdI_2-type $FeCl_2$ will transform to a more stable *Pnnm* structure at 10.8 GPa. The predicted new phase, however, is found to be eneretically unstable against decomposition into Fe and $FeCl_3$. For FeI_2, even though the CdI_2-type structure were found experimentally to exist up to 70 GPa the calculations predicted a Pa$\bar{3}$ structure becomes more stable at 70 GPa. No experimental structural study has been performed on the Fe-Br system at high pressure. At extremely high pressure, theoretical calculations have uncovered new stable phases at different stoichiometries for FeCl, Fe_2Br and Fe_2I, with the CsCl, *Pnma* and *P*6_3/*mmc* space group symmetries, respectively. The theoretical results show the high-pressure phase diagrams of iron-halides are very rich thus encourage more experimental studies to verify the predicted new phases and structural transformations.

At a given pressure, the convex hull plot connects phases that are stable against decomposition into the elements or a mixture of compounds with different stoichiometries. Stable structures for FeCl, Fe_2Br and Fe_2I are found at 360 GPa. It is no surprise that at high pressure the structures of the polymorphs are very different from those exist at lower pressures, as pressure can dramatically alter the electronic structure of a material. Indeed, the basic octahedron building unit prevailing in FeX_n at lower pressures no longer exist. The most stable crystalline phase of the Fe-Cl system is FeCl having a CsCl space group at 360 GPa. This is reminiscent of the Fe-Si system in which the most stable phase is a CsCl-type FeSi. Experiment has also shown at Earth's core conditions the CsCl-type FeS is most stable. A predicted stable CsCl- FeCl may add to the list that chloride may incorporate it into Fe and stabilize body-centered cubic structure at Earth's inner core pressure. As a result of compression, the coordination number of Fe increases from six in the low-pressure structure to eight in the CsCl-type structure. In comparison, the situation is rather different in orthorhombic Fe_2Br, the most stable phase of the Fe-Br system at 360 GPa. In this structure, half of the Fe atoms coordinated with two Br atoms at a Fe-Br distance of 2.04 Å, while the rest are surrounded by 4 Br at distances from 2.02 Å - 2.04 Å. The structure of the hexagonal Fe_2I is more interesting. In this structure, there are two crystallographically inequivalent Fe atom at the Wyckoff's 2a and 2c sites. At the 2c (0.667, 0.333, 0.75) sites, the Fe is bonded with three nearest iodine atoms with a Fe-I bond of 2.05 Å and forming graphene-like layers perpendicular to the *c* axis. These layers are arranged in such a way that the Fe (or I) atoms in one layer lay atop of the I (or Fe) atoms in the adjacent layer suggesting the layers are connected through Fe-I bonds with a bond length of 2.18 Å, the separation between the layers. Thus, each Fe atom is coordinated with three I atoms in the plane and two I atoms above and below it forming trigonal pyramids. On the other hand, Fe atoms situated at the Wyckoff 2a (0,0,0) sites form one dimensional chains with Fe-Fe bonds of 2.18 Å running parallel to the *c* axis through the center of the rings of the hexagonal layers. Therefore, the structure is best described as a network of edge-shared Fe-I trigonal bipyramids with linear Fe chains running down the voids along the *c*-axis.

Now we discuss the stability of the predicted structures. The most stable phases of each stoichiometry are indicated by the lowest points on the convex-hull for each pressure. The convex-hull plots show a clear trend in the chemical evolution of the iron halides under pressures. At lower pressures (≤ 35 GPa for I and Br and ≤ 70 GPa for I), halogen-rich compounds are stable while the iron-rich phases are unstable. The reverse trend is predicted at 360 GPa as FeX or Fe_2X became most stable phases. The results are different from the iron-silicon system where only one stoichiometry, the CsCl-type FeSi is found to be stable. Therefore, iron-halides at inner Earth's pressure exhibit much richer phase varieties. At the low-pressure regions of the convex-hull plots of chloride to bromide to iodide, the enthalpy difference between the compounds and the elements decrease, indicating decreasing stability of the iron-halides. For iodine at 360 GPa, a deeper convex-hull is observed suggesting that the iron-iodide at Earth's inner core pressure is more stable relative to the chlorides and bromides. This observation may indicate different bonding in Fe_2I. As shown in the convex-hull plots, the enthalpy difference between the Fe-halides and the constituent elements are generally larger at high pressures than at lower pressures. This might suggest that these binary halides may be stabilized at the Earth's core pressure.

To characterize the bonding of the high pressure iron-halides, Bader quantum theory of atom-in-molecule (QTAIM) analysis was performed. In this method, an atom in a molecule or a crystal is unambiguously defined by the region enclosed by the zero flux surfaces and the charge density is a minimum perpendicular to the surface. The electronic charge on the atom is obtained from integrating the charges in each atomic region. Recently, this method was successfully used to characterize the structure of the oxide glasses of Si and metallic alloys at high pressures. The Bader charges of Fe and the halogens in FeX_n compounds are listed in Table IV. Charge transfers between halogen atoms and iron atoms are observed. For FeX_2 and FeX_3, electrons are transferred from the iron atoms to halogens but the magnitude decreases from chlorides to bromides to iodides following the electronegativity of the halogens. The number of electron transferred parallels with the order of stability of the iron-halides as indicated by the enthalpy differences. This suggests that ionic bonding plays a key role in stabilizing the halide even at moderate high pressures. As the pressure is increased, the electron donated by Fe becomes smaller. As the stable phase switches from halogen-rich to iron-rich region, such as in FeI_2 and FeI_3 at high pressures, the number of charge transferred between Fe and I is very small indicating very weak ionic bonds. However, upon further compression, in FeI and Fe_2I, the Fe atoms are found to be an electron acceptor by receiving electrons from the iodine! The reversal is not uncommon at high pressure and has been previously reported in CsI.

Extending the calculated trend in the convex hull of iron- chlorides and bromides, one would anticipate that iodides at 360 GPa to have a shallower convex hull. Instead, an even much deeper one is found. We attribute the apparent discrepancy to gain in energy of the Fe-iodides from substantial changes in the electronic structure. As indicated from the Bader charge analysis, in Fe_2I, the stabilization of the crystal is through “covalent” interaction between the Fe and I atoms instead of charge-transfer from Fe atoms. The covalent bonding is reflected in the very different structure of Fe_2I on the formation of planar graphene-like layers connect through weak Fe-I bonds. This suggestion is confirmed by a thorough toplogical analysis of the electron density of Fe_2I according to the QTAIM. Bond critical pointsare found in all closet Fe-I contacts in the trigonal bipyramids but, surprisingly, also between the I atoms and the Fe forming the linear chains!

The theoretical results reported here indicate iron-halides could be stable at Earth's core. During the Earth's initial formation stage, the interior pressure is several tens of GPa, much lower than the present-day Earth's core. The theoretical results show iron-halides can exist in the form of halogen-rich phases at low pressures (< 100 GPa), therefore, it is plausible that some iron-halides formed in the early stage may be sequestered into the core. However, as the Earth gradually grew and the pressure increased, the iron-halides would experience chemical evolution with the release of excess halogen to meet the stiochiometric requirement on the chemical stability leaving iron-rich halides in the present-day Earth's inner core. This conclusion adds to other possible ways to explain the missing halogen paradox. It is prudent to point out that the energetic of the predicted structures are performed athermally (*i.e.* 0 K). It is expected the temperature in the Earth’s interior core may influence the structures. Furthermore, iron-halides may also exist as non-stoichiometric alloys. This topic is beyond the scope of this work.

Recently, the structure of FeO_2 near the lower mantle pressure (*ca.* 80 GPa) has been resolved. This observation raised the possibility than Fe in the oxide minerals under high pressure may adopt a “formal” +4 oxidation state (OS), contrary to the common believe that the Fe OS should decrease with increasing pressure. The existence of highly oxidized Fe minerals is highly significant as it may alter the estimation of the oxygen budget, and as mentioned above, also affect the distributions of volatile elements. Therefore, it is relevant to comment on the evolution of the Fe OS in the most stable structure(s) of the iron-halides at a given pressure. At 25 GPa. The convex-hull plots for FeX_n: X= Cl, Br and I show the FeX_3 structure with Fe(III) is most stable at 25 GPa. From 70 - 135 GPa, FeX_2 becomes more stable for all the halides and the OS of Fe is formally Fe(II). At 135 GPa, The most stable forms of FeX_n are rich in Fe and so the formal OS is close to Fe(0). The trend Fe(II) → Fe(III) → Fe(0) with increasing pressure is, therefore, followed in the iron-halide systems.

4. Conclusion

In conclusion, we have systematically investigated structural property and phase stability of iron halides at pressures from Earth's upper mantle down to Earth's inner core with First principles structure prediction calculations. The theoretical results reveal that different stoichiometric Fe-halides can exist at different depth of the Earth's region. At the core pressure, iron-rich halides are the most stable phases. It is found that pressure plays a key role in determining the stoichiometry and the structure of the iron halides as in the formation of Fe2I with a novel structure composed of graphene (Fe-I) hexagonal sheets penetrated by linear chains of Fe atoms. The results suggest the possibility of the existence of halogen-rich iron halides during the Earth's initial accretion stage and lower the volatility of the halogens. In the subsequent process(es) to the formation of the present core, these iron halides may be sequestered into the core and, with the increase of pressure and to maintain chemical stability, halogen maybe released.

5. Schedule and prospect for the future

I have been a Hokusai general user and wish to continue using the system. During the last fiscal year 2017, I have finished the studies on the high-pressure behavior of FeXn (X=Cl, Br and I, n

=1/4, 1/3,1/2, 1, 2, 3, 4), and our manuscript on this work is to be submitted. For the next fiscal year 2017, we plan to continue using Hokusai supercomputer to study the high-pressure structural and electronic properites of MPN_2 with M being Li, Na and Cu through CALYPSO code, and build the high-pressure phase diagram. We expect high standard publications can be eventually achieved.