Based on the hard-soft acid-base (HSAB) theory, the metallogenic specificity of magmatic hydrothermal ore deposits can be explained by the maximum hardness principle (MHP) and the minimum electrophilicity principle (mEP), which govern the reactions between the ore-forming cations and the anions from magmatic fluid phase. According to the HSAB theory, fluorine is a hard base with high electrophilicity and hardness, it attracts the hard acid ions such as tungsten (W) and tin (Sn); on the other hands, sulfur is a soft base with low electrophilicity and hardness, it attracts the soft acid ions such as copper (Cu) and gold (Au); meanwhile, chlorine exhibits intermediate characters, so it attracts the borderline ions such as rare earth elements (REE), and gold. Overall, the hardness of the hydrothermal fluids bearing ions such as F, Cl, and/or S is always higher than that of the silicate melts, accordingly, the magmatic fluid can segregate the ore-forming metals from the melts during the hydrothermal stage of magmatic system evolution. The felsic magmas generated in the collisional setting contain much fluorine, so these melts can attract the hard acid ions (W and Sn) from the source to form the W and/or Sn ore deposit. However, the arc magmas contain much higher sulfur content, and they attract the soft acid ions (Cu, Au) from the source to form the porphyry deposits. The chlorine and/or CO₂, are enriched in the alkaline magmas generated in the intraplate extensional setting, therefore, these magmas attract the ions of Fe, Au, and REE from the environment to form the iron oxides-copper-gold (IOCG) deposits.

**Key words:** hard-soft acid-base theory, chemical hardness, electronegativity, ore formation

The hard-soft acid-base (HSAB) theory classifies elements into acid (the electrons acceptors) and base (the electrons donors) categories, almost all the compounds can be regarded as the products of acid and base (Pearson, 1997). Combining the HSAB theory with geochemistry opens a brand new way to understanding the ore formation and the metallogenic specificity of magmatic hydrothermal deposits.

Chemical activity of the acid/base can be described by electronegativity, chemical hardness and electrophilicity, which are basic parameters in the HSAB theory (Pearson, 1997). Electronegativity represents the ability of an atom in a molecule to attract electrons. High electronegativity means the atom is more capable of attracting electrons. Chemical hardness represents the ability of an ion to resist the transferring of electron, softness is the inverse of hardness. Electrophilicity determines the capacity of one element to promote a softer or covalent reaction. The electrophilicity of an ion/cation are determined by its electronegativity and chemical hardness.

According to the values of electronegativity, chemical hardness and electrophilicity, both of acid and base can be divided into three categories: hard, soft and borderline. An ion with intermediate values are classified as borderline acid/base. The chemical hardness and electronegativity of the metals having several oxidation states increase in harmony with the valence number. The univalent metals with relatively low hardness are considered as soft acid. The bivalent metals are considered as borderline with intermediate electronegativity and hardness. The metals with high valences are hard acid. The electrophilicity of cation is positively correlated to its valence state. The electrophilicity of most univalent metals is about 10 eV, and that of bivalent metals increases from 25 eV to 60 eV, while it reaches a higher range of 50 eV to 110 eV for trivalent metals. Fluorine represents the typical hard base with high electronegativity and chemical hardness of 10.4 eV and 7 eV, respectively. The chemical hardness of sulfur is low, in range of 5.5 eV to 3.9 eV due to its diverse chemical valences and compound styles, therefore sulfur is a soft base. However, chlorine has relatively higher...
The electronegativity of 8.3 eV but lower chemical hardness of 4.7 eV.

The reaction between acid and base obeys the maximum hardness principle (MHP) and the minimum electrophilicity principle (mEP). The MHP indicates that molecules arrange themselves to be as hard as possible (Pearson and Chattaraj, 2008), it means that a hard-soft element pair react with another soft-hard pair to yield two new species with hard-hard and soft-soft combinations. The mEP demonstrates that ions with high electrophilicity are preferential to react with atoms with low electrophilicity (Chamorro et al., 2003). When the acid and the base have approximate electronegativity, the reaction system should reach the maximum hardness and the minimum electrophilicity.

The electronegativity, hardness and electrophilicity of the complex system such as magma can be represented by the geometrical averages of their components. Owing to the high chemical hardness of SiO₂, felsic magma is hard, meanwhile the ratio of electrophilicity(ω) and hardness(η), ω/η of the felsic magma is less than 1. However, mafic and ultramafic magmas exhibit higher electrophilicity but lower hardness due to their high contents of MgO, FeO, and TiO₂. The ω/η ratios of the mafic and ultramafic magmas are greater than 1. Alkali oxides such as K₂O, Na₂O exhibit lower hardness and have ω/η ratio < 1. The electrophilicity and hardness of alkaline magma are determined by the proportion of SiO₂ and alkali oxides. According to the MHP and the mEP, the felsic magma, which is chemically hard, is prior to attract the hard ions as F⁻, W⁶⁺, and Sn³⁺. The felsic alkaline magma has higher hardness, and can attract hard ions such as CO₂, REE³⁺; but the mafic alkaline magma or the peralkaline magma exhibit lower hardness and low electrophilicity, so they mainly attract the soft ions such as Cl⁻, Cu²⁺, and Au⁺. On the other hand, the mafic magma exhibits higher electrophilicity but lower hardness, so it mainly attracts soft base such as S, and soft metals such as Cu⁺ and Au⁺.

From the view of hard-soft acid-base concept, the fluid phase released from magmatic system is much harder than the silicate melts, because the ions dissolved by the fluid phase such as F⁻, Cl⁻, S⁻, S²⁻, and CO⁻ are chemically much harder than the silicate minerals. The equivalent electronegativity, hardness and electrophilicity of the fluid can be represented by the geometrical averages of these ions. Semi-quantitative computation shows that once the volatile content of halogens increases by an order of magnitude, the hardness and electrophilicity values of the fluid changed significantly (Fig. 1). As shown in the Figure 1, fluorine can increase the hardness and the electrophilicity of fluid progressively, but the sulfur will decrease both; otherwise, chlorine can increase the electrophilicity, but decrease the hardness of the fluid. Ore-forming metal ions have much higher hardness than those of the fluid and magma, accordingly, the metal ions will be attracted by the volatile-rich fluid, which is separated from the magma during the volatile boiling stage (Vigneresse, 2009; Wang and Cheng, 2011; Jiao and Wang, 2012).

It is well known that the different type magmatic hydrothermal deposits concentrate different kind ore-forming metals, and this phenomenon is called the metallogenic specificity. This phenomenon can be explained from the view of HASB concept. The hydrothermal fluid released by mafic magma, which contains more sulfur than other type magmas, has lower chemical hardness and electrophilicity values, and it prefers to dissolve the soft metal ions such as Cu⁺ and Au⁺ to form the porphyry Cu-Au deposits. Meanwhile, the fluorine-rich felsic magma will expel the fluid with high electrophilicity and hardness values. This kind of fluid is easier to dissolve the hard metals such as W and Sn for mineralization. However, the chlorine-rich fluid released by some alkaline magma has low hardness but high electrophilicity, accordingly, the chlorine-rich fluid can extract the soft/borderline metals with the low electrophilicity such as Cu⁺, Fe²⁺, Au⁺, and Ag⁺ for mineralization. The CO₂-riched fluid from mantle-derived alkaline magma has high hardness but low electrophilicity with ω/η < 1. In this case, the chemical reactions will be controlled by the MHP, and the fluid prefers to extract the hard metals such as REE³⁺ for mineralization.
We calculate the hardness and electrophilicity of the hydrothermal fluids for several typical ore deposits (Fig. 2). The result shows that the hardness and electrophilicity of the hydrothermal fluids from the W and/or Sn deposits are much higher than those of the neutral fluid (water) due to the high fluorine content in the magma. Compared to the neutral fluid, the hydrothermal fluids of the porphyry-type copper deposits exhibit lower values of hardness and electrophilicity as a consequence of the sulfur enrichment in the magma. For the chlorine-rich hydrothermal fluids of IOCG-type deposits, they have higher electrophilicity but lower chemical hardness values than those of the neutral fluid.

In summary, the felsic magma generated in the collisional orogenic setting is F-rich, and has high chemical hardness which is advantageous for the tungsten and/or tin mineralization; and the S-rich mafic magma originated in the intraplate extensional background. The hard-soft acid-base theory provides a sound chemical reliance to understand the metallogenic specificity of magmatic hydrothermal deposits.

References