

# Relationship between cation distribution with electrochemical and flotation properties of calcic amphiboles



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## ABSTRACT

Reverse cationic flotation is a very efficient method of beneficiation of oxidised iron ores when you need to separate hematite and quartz. This method can be also applied to reduce silica content in the magnetite concentrates obtained by wet low-intensity magnetic separation. However, cationic flotation in this case is less effective due to the presence of Fe–Mg–Al-bearing silicates as amphiboles in magnetite ores. These silicates are concentrated in magnetic products and determine the difficulties of their separation from iron oxides when amines and starches are used as collectors and depressants, respectively. The recalculation of the results of the electron microprobe analysis of five calcic Fe–Mg–Al-bearing amphiboles used to characterise cation distributions in structural units and to obtain structural formulae in accord with stoichiometric limits was conducted. The Mössbauer spectroscopy was used to examine the validity of the empirical estimation of cation distributions in amphiboles. The studied samples are metamorphic pargasite, ferrotschermakite and magnesiohornblende and volcanic kaersutite and magnesiohornblende. The crystallographic analyses of the amphibole samples exhibited their heterogeneous surfaces explaining worse floatability of amphiboles with amines at pH 10. The electrokinetic measurements showed that the position of the isoelectric point of amphiboles is related to a substitution of  $Al^{3+}$  for  $Si^{4+}$  in tetrahedral sites and to an amount of  $Mg^{2+}$  cations in octahedral sites. Thus, the amine adsorption onto amphiboles through electrostatic interactions is mainly affected by a distribution of these cations in tetrahedral and octahedral sites of amphiboles. In addition, the effect of starch on the depression of Fe–Mg–Al-bearing amphiboles during flotation can be attributed to the presence of metal ions on the amphibole surface, which are capable of forming strong chemical complexes with starch molecules.

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## 1. Introduction

Iron formations are the most important sources to economic iron ore deposits, which account for the majority of current world iron ore production. Iron formations are from the Early Proterozoic or Achaean. However, a part of iron formations is from the Late Proterozoic or Early Palaeozoic. Most are banded and are known as Banded Iron Formations (BIFs).

In general, iron formations can be divided into three major classes: (1) unenriched primary iron formations with typically 30 to 45% Fe; (2) martite–goethite ores formed by supergene processes, with abundant hydrous iron oxides containing 56 to 63% Fe; (3) high-grade hematite ores are of supergene modified hypogene or metamorphic origin with 60 to 68% Fe (Morris, 1985; Clout and Simonson, 2005).

High-grade hematite ores can be further subdivided into hematite and microplaty hematite ore types (Spier et al., 2003). The Carajás and Quadrilátero Ferrífero provinces in Brazil as well as the Hamersley province in Australia are among the largest formations of martite–goethite and high-grade hematite ores. In contrast, unenriched primary iron formation hosted iron ores included both magnetite- and hematite-rich ores are practically mined in the United States, Canada and especially in China and Russia. Iron formation hosted iron ores are usually located in greenschist- to amphibolite-facies terranes (Neal, 2000). The ore zone of greenschist-facies contains very fine grained magnetite or very fine gangue inclusions in magnetite, whereas amphibolite-facies with the higher metamorphic grade associated with coarser magnetite grain size and more discrete grains of gangue. The main ore mineral is magnetite, although it has been oxidised to martite near surface. Actually martite is usually used term to denote hematite pseudomorphs after magnetite. The gangue mineralogy is very complex and generally includes quartz, muscovite, biotite, stilpnomelane, chlorites, albite, Fe-bearing carbonates, calcite and amphiboles of the Mg–Fe–Mn–Li, sodic and calcic groups as cummingtonite, grunerite, riebeckite, arfvedsonite,

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actinolite–tremolite and hornblendes as independent or composite bands. In fact, Mg–Fe–Mn–Li and sodic amphiboles are indicators of high-grade iron ore, whereas calcic amphiboles are indicators of low-grade iron ore.

Reverse cationic flotation remains the most popular flotation route used in the iron ore industry (Filippov et al., 2014). However, few studies are available regarding the flotation separation of amphiboles from iron oxides. In fact, Fe-bearing amphiboles are strongly concentrated in the iron magnetic concentrates and further are weakly floated by cationic collectors (Filippov et al., 2010). Additionally, then starch is used as a depressant of iron oxides the floatability of Fe–Mg–Al-bearing calcic amphiboles is more impaired. Infrared and X-ray photoelectron spectrometry studies confirmed that the effect of starch on the depression of Fe–Mg–Al-bearing amphiboles during flotation can be attributed to the presence of metal ions on the amphibole surface, which are capable of forming strong chemical complexes with starch molecules (Filippov et al., 2013).

The main goal of the investigations presented in this paper was to find an interrelation between surface crystal chemistry of calcic amphiboles and their electrochemical and flotation properties.

2. Background

Amphiboles are inosilicates with a basic structural unit (Si<sub>4</sub>O<sub>11</sub>)<sup>6-</sup> consisting of interlocked double chains of silicate tetrahedrons T(1)–T(2) (Fig. 1). The T(1) and T(2) silicate tetrahedrons are bound together through two bridging basal oxygens O(5) and O(6).

The T(1) silicate tetrahedrons are bound together in a chain through the bridging basal oxygen O(7). The chains of silicate tetrahedrons in turn are bound through the apical oxygens O(4) with the chains of cations in octahedral coordination, which form nonequivalent M(1), M(2) and M(3) sites. Thus, the double chains of silicate tetrahedrons in the crystal structure of amphiboles are bonded each to other laterally through the octahedral strips. The M(1) and M(3) sites are bound

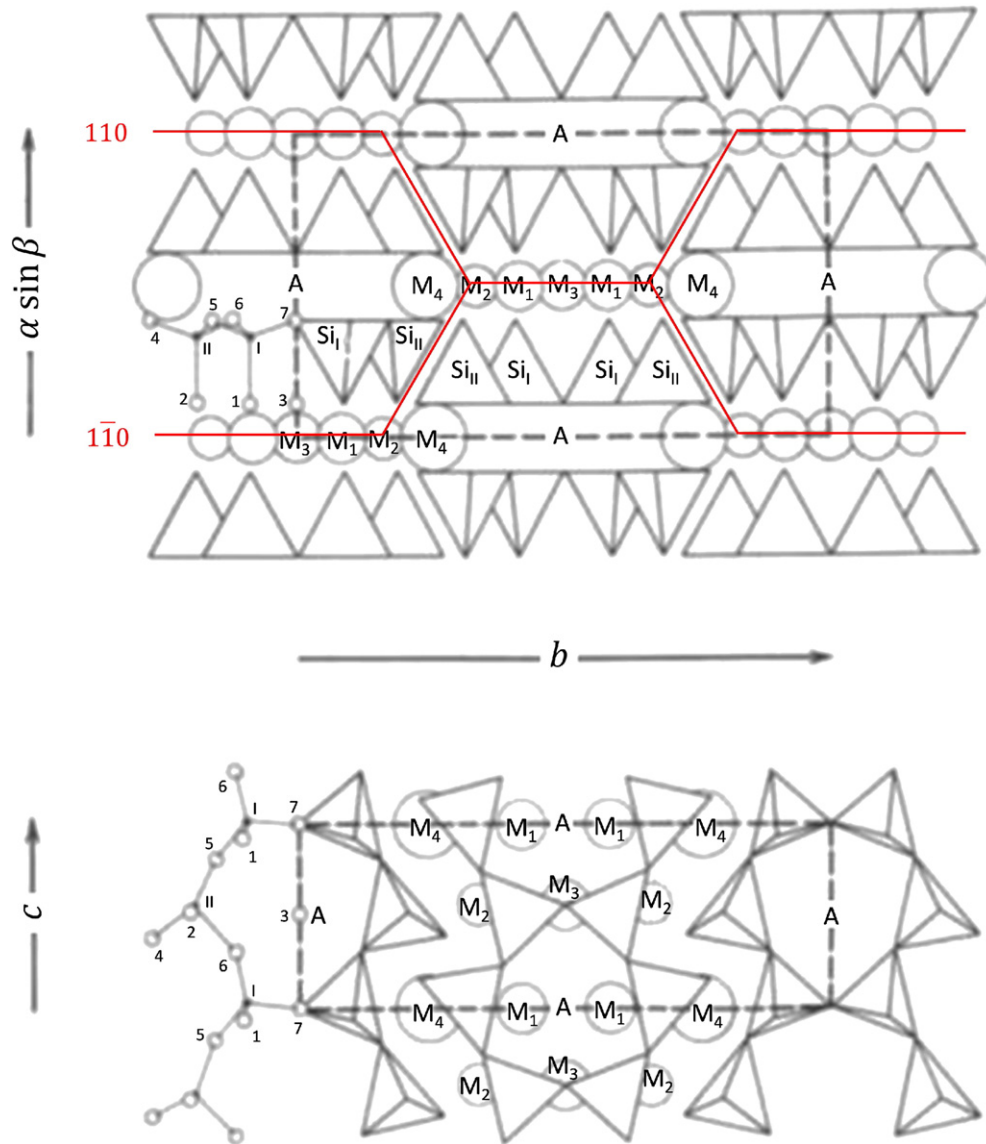


Fig. 1. Schematic diagrams of monoclinic amphibole structural elements. The tetrahedral sites are shown as tetrahedrons, triangle and small solid circles and designated Si<sub>I</sub> and Si<sub>II</sub> or I and II. The octahedral sites are represented by circles M1, M2 and M3. The six-eight-fold coordinated cations are represented by large circles M4. The cations in 10–12-fold coordination are represented simply by the letter A. Anion positions are shown by small open circles designated from 1 to 7. The unit cell is separated by a dash-dotted line. Red lines show the cleavage planes [adapted from Colville et al. (1966)].

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