



## Research paper

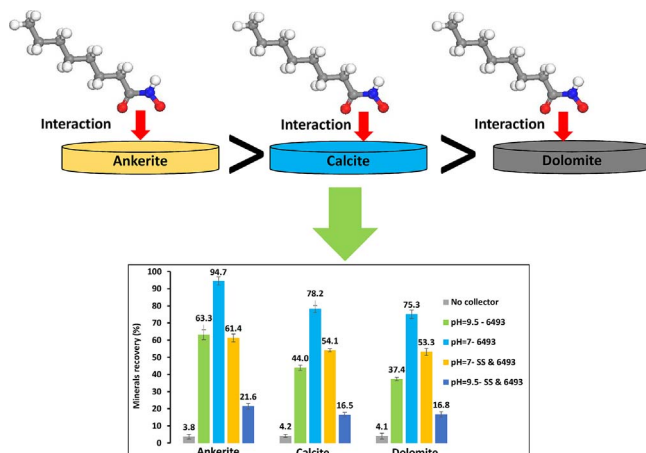
## Surface interactions and flotation behavior of calcite, dolomite and ankerite with alkyl hydroxamic acid bearing collector and sodium silicate



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## GRAPHICAL ABSTRACT



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## ABSTRACT

The surface interactions and adsorption mechanism of alkyl hydroxamic acid bearing collectors and sodium silicate depressant on common carbonatite gangue minerals, including calcite, dolomite and ankerite in flotation were investigated. For this purpose, firstly the flotation behaviors of these minerals in the presence of the collector and depressant were investigated *via* micro-flotation tests at pH 7–9.5. Meanwhile, the interaction nature of this collector and depressant with minerals was disclosed through FTIR and zeta potential measurements over the studied pH range. It was found that either floatability of minerals in the presence of collector or the affinity of minerals towards collector and depressant adsorption are in the order of ankerite > calcite > dolomite. The nature of collector-minerals' interactions and also the collector's adsorption mechanism were further studied *via* density functional theory (DFT) simulations to identify the likeliest collector configurations and adsorption pathways of collector and depressant on the mineral surfaces. It was concluded that ankerite has higher affinity towards alkyl hydroxamic acid collector and also sodium silicate as compared with calcite and dolomite. It was revealed that collector is going to interact with metal atoms on the minerals surfaces via covalent bonding through which bridged and monodentate binding configuration are more favorable. It was found that Fe atoms on the mineral surfaces are more involved in bond formation as compared with Ca and Mg. The DFT simulations also indicated that sodium silicate has more affinity towards ankerite which was confirmed *via* experimental observations. Besides, the surface interaction pathway of both  $\text{SiO}(\text{OH})_3^-$  and  $\text{Si}(\text{OH})_4$  as dominated silicate monomers in aqueous phase on the mineral surfaces were demonstrated. It was found  $\text{SiO}$

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$(\text{OH})_3^-$  species enable either covalent or hydrogen bonding on the mineral surfaces, while  $\text{Si}(\text{OH})_4$  species are likely to interact with minerals only through hydrogen bonding. Therefore,  $\text{SiO}(\text{OH})_3^-$  species are corroborated to prompt more important depressant effects on froth flotation of carbonatite gangue minerals.

## 1. Introduction

As a well-trodden separation route, froth flotation is undoubtedly “*La voie royale*” mineral processors extensively rely on for the beneficiation of a multitude of complex ores [1]. This method is based on the separation of valuable minerals from their associated gangue minerals by considering differences inherent to their *surface* physicochemical properties [1,2]. Since its early commercial applications traced back to *ca.* 1905, froth flotation has significantly progressed in terms of process, equipment and reagents, and has become nowadays the plough-horse of the mineral processing industry [3,4]. Recently, the trend towards processing low-grade complex ores has increased considerably as a consequence of depletion of high-grade ores. This negative evolution in the quality of raw materials is not without consequences on the performance of flotation-based mineral processing methods. Indeed, separation of valuable minerals from their associated gangue minerals has been a critical issue especially in froth flotation because of similarity between gangue and valuable minerals’ surface properties [1].

As a matter of fact, gangue minerals’ behavior in froth flotation in terms of interaction with various reagents and surface chemistry can neither be devolved to the second role nor overlooked in the selection of the best process operating window of froth flotation. In this regard, carbonatite gangue minerals, such as calcite and dolomite, have been more critical as they represent the most abundant gangue minerals [5–9]. They are found in association with various valuable minerals, such as apatite [5,10–12], niobium minerals [6,13,14], sulfide minerals [7,8], oxidized zinc minerals [15], smithsonite [16,17], fluorite [18,19], scheelite [12,20], celestite [21], gold ores [22], rare earth minerals [23–28], phosphate ores [29,30], cassiterite [31], wolframite [32], hematite [33], and so forth. Thus, they can significantly affect the flotation of various valuable minerals. Carbonatite gangue minerals can also lead to operational problems such as in preg-robbing [22,34] and acid consumption [35] in mineral post-flotation leaching. Therefore, study of their behavior in froth flotation is compulsory in order to provide meaningful insights to improve flotation recovery and selectivity of the valuable minerals embedded with carbonatite gangues.

In this regard, the interaction nature as well as flotation recovery of carbonatite gangue minerals in the presence of most important reagents, *i.e.*, collectors and depressant, used in the flotation of valuable minerals can be a crucial point. Hydroxamic acid-bearing collectors are viewed as a family of effective collectors for the flotation of various oxides and sulfide minerals [36]. Likewise, sodium silicate has been known as one of the most important depressants for carbonatite gangue minerals and is widely

used as such in many flotation systems treating pulps containing these gangue minerals [1,37]. Understanding the interactions that these two types of reagents develop with carbonatite gangue minerals is compulsory to improve flotation recovery of the valuable target minerals.

However, in spite of several studies have trickled to the open literature over the past years, understanding the flotation of carbonatite gangue minerals is still in need of refinements. In this regard, molecular and quantum mechanical simulations based on density functional theory (DFT) can be considered as opportune tools to study the electronic interactions between the various reagents and minerals in the context of froth flotation. DFT simulations are indeed very powerful to unveil new molecular-level insights regarding the interactions of collector and depressant with minerals [38–40]. Therefore, integrated approaches merging experimental observations with DFT simulations are purported to be of superior value to help grasping the phenomenology of carbonatite gangue minerals flotation.

The present study’s endeavor is to investigate experimentally and through DFT simulations the nature of interactions of sodium silicate depressant and alkyl hydroxamic acid bearing collectors with the most common carbonatite gangue minerals, *i.e.*, calcite, dolomite and ankerite. For this purpose, micro-flotation tests, zeta potential measurements and FTIR analyses were carried out to establish the affinity of the three carbonatite minerals towards alkyl hydroxamic acid collector as a function of pulp pH. The role of silicate speciation as a function of pH in weakening (or suppressing) the interaction between collector and carbonatite minerals was also investigated. Furthermore, DFT simulations helped rationalize the experimental observations in terms of interaction energies and adsorption configurations of both collector and depressant with the mineral surfaces. It is therefore expected that the findings from the present study will prove useful for improving the flotation performance of a wide range of valuable minerals associated with carbonatite gangue minerals where industry relies on the use of alkyl hydroxamic acid bearing collectors and sodium silicate in their various flotation processes.

## 2. Materials & methods

### 2.1. Minerals

Three different single carbonatite minerals, namely, calcite and dolomite (from Québec Province, Canada kindly provided by the Department of Geology at Laval University) and ankerite (from Cow Green, Teesdale County, Durham, England) were acquired. The X-ray powder diffractograms of these single minerals are illustrated in Fig. 1.

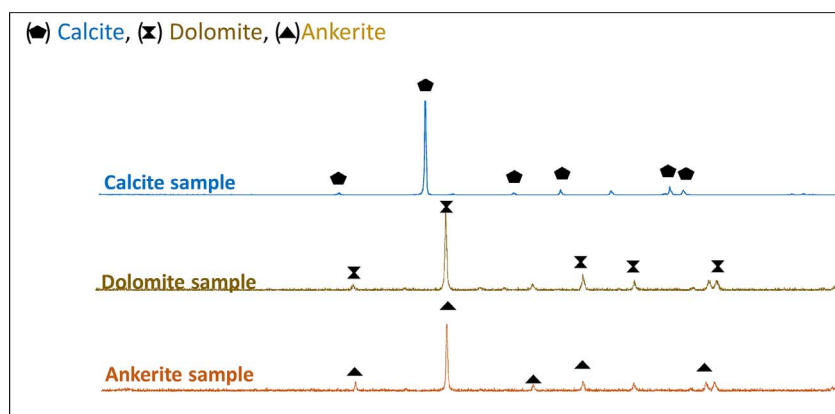


Fig. 1. Powder X-ray diffraction patterns of model single-minerals including calcite, dolomite and ankerite samples.

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