Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 74 (2010) 634–644

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

# Micro-scale S isotope studies of the Kharaelakh intrusion, Noril'sk region, Siberia: Constraints on the genesis of coexisting anhydrite and sulfide minerals

Edward M. Ripley [a,*], Chusi Li [a], Craig H. Moore [a], Axel K. Schmitt [b]

[a] *Department of Geological Sciences, Indiana University, Bloomington, IN 47405, United States*
[b] *Department of Earth and Space Sciences, University of California, Los Angeles, Los Angeles, CA 90095, United States*

Received 4 June 2009; accepted in revised form 28 September 2009; available online 7 October 2009

---

## Abstract

The coexistence of magmatic anhydrite and sulfide minerals in non-arc-related mafic magmas has only rarely been documented. Likewise the S isotope fractionation between sulfate and sulfide in mafic rocks has infrequently been measured. In the Kharaelakh intrusion associated with the world-famous Noril'sk ore district in Siberia coexisting magmatic anhydrite and sulfide minerals have been identified. Sulfur isotope compositions of the anhydrite–sulfide assemblages have been measured via both ion microprobe and conventional analyses to help elucidate the origin of the anhydrite–sulfide pairs. Magmatic anhydrite and chalcopyrite are characterized by $\delta^{34}$S values between 18.8‰ and 22.8‰, and 9.3‰ and 13.2‰, respectfully. Coexisting anhydrite and chalcopyrite show $\Delta$ values that fall between 8.5‰ and 11.9‰. Anhydrite in the Kharaelakh intrusion is most readily explained by the assimilation of sulfate from country rocks; partial reduction to sulfide led to mixing between sulfate-derived sulfide and sulfide of mantle origin. The variable anhydrite and sulfide $\delta^{34}$S values are a function of differing degrees of sulfate reduction, variable mixing of sulfate-derived and mantle sulfide, incomplete isotopic homogenization of the magma, and a lack of uniform attainment of isotopic equilibrium during subsolidus cooling. The $\delta^{34}$S values of sulfide minerals have changed much less with cooling than have anhydrite values due in large part to the high sulfide/sulfate ratio. Variations in both sulfide and anhydrite $\delta^{34}$S values indicate that isotopically distinct domains existed on a centimeter scale. Late stage hydrothermal anhydrite and pyrite also occur associated with Ca-rich hydrous alteration assemblages (e.g., thomsonite, prehnite, pectolite, epidote, xonotlite). $\delta^{34}$S values of secondary hydrothermal anhydrite and pyrite determined by conventional analyses are in the same range as those of the magmatic minerals. Anhydrite–pyrite $\Delta$ values are in the 9.1–10.1‰ range, and are smaller than anticipated for the low temperatures indicated by the silicate alteration assemblages. The small $\Delta$ values are suggestive of either sulfate–sulfide isotopic disequilibrium or closure of the system to further exchange between ~550 and 600 °C. Our results confirm the importance of the assimilation of externally derived sulfur in the generation of the elevated $\delta^{34}$S values in the Kharaelakh intrusion, but highlight the sulfur isotopic variability that may occur in magmatic systems. In addition, our results confirm the need for more precise experimental determination of sulfate–sulfide sulfur isotope fractionation factors in high-T systems.

---

## 1. INTRODUCTION

Recently Li et al. (2009a) showed that magmatic anhydrite is present in mafic rocks of the Kharaelakh intrusion in the Noril'sk area of Siberia. They utilized the presence of anhydrite and the isotopic composition of sulfide minerals in the construction of a mass balance model to illustrate the large quantities of sulfur that could have been released during Permo-Triassic flood basalt volcanism, and that therefore may have been of significance in mass extinction events (e.g., Campbell et al., 1992; Renne et al., 1995; Reichow et al., 2009). Assimilation of sedimentary sulfate

---

[*] Corresponding author. Tel./fax: +1 812 855 1196.
*E-mail address:* ripley@indiana.edu (E.M. Ripley).

0016-7037/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.gca.2009.10.003

by mafic magmas in the Noril'sk area has also been proposed as a key process for the production of the world-famous Ni–Cu–PGE ores that are associated with differentiated sills (e.g., Naldrett, 1992; Arndt et al., 2003; Li et al., 2003, 2009b; Lightfoot and Keays, 2005). The identification of magmatic anhydrite that coexists with sulfide minerals in the gabbroic rocks of the Kharaelakh intrusion permits an evaluation of the isotopic characteristics of coexisting sulfate and sulfide at magmatic temperatures. The presence of sulfate and sulfide species in basaltic magmas has been described by Sakai et al. (1982), but has not been commonly reported in mafic plutonic rocks. The potential importance of oxidized sulfate-bearing magmas in the generation of porphyry Cu–Mo deposits has been recognized for some time (e.g., Burnham, 1979; Burnham and Ohmoto, 1980; Sillitoe, 1997; Streck and Dilles, 1998; Mungall, 2002; Seedorff et al., 2005). Transfer of oxidized S to an exsolving vapor phase, followed by partial hydrolysis of sulfate to $H_2S$ generates the reduced S that is necessary for the precipitation of Cu–Mo sulfide minerals. Experimental studies have shown that oxidized magmas may dissolve up to an order of magnitude more S than reduced magmas (e.g., Luhr, 1990; Jugo et al., 2005).

Sakai et al. (1982) reported sulfur isotopic differences between sulfate and sulfide ($\Delta$(sulfate − sulfide)) in Hawaiian basalts that range between 6‰ and 9‰. They proposed that sulfate–sulfide isotopic equilibrium was achieved at temperatures near the solidus temperature of ~980 °C. Sulfur isotope fractionation between sulfate and sulfide at high temperatures has been experimentally studied by Miyoshi et al. (1984) who decomposed anhydrous $Na_2SO_3$ in NaCl and LiCl–KCl melts. Fractionation between anhydrite and sulfide minerals at high temperatures can also be estimated using lower-temperature (<400 °C) experimental data summarized in Ohmoto and Lasaga (1982). Our results are evaluated in the light of available fractionation factors, although the values determined by Miyoshi et al. (1984) and Ohmoto and Lasaga (1982) differ from those obtained by Sakai et al. (1982). Our studies of the S isotope compositions of coexisting anhydrite and sulfide in the Kharaelakh intrusion were initiated to constrain the origin of sulfate and sulfide in the gabbroic rocks. In addition the micro-scale analyses were conducted to determine if sulfate–sulfide isotopic equilibrium was attained and if so at what temperature and over what length scale. Due to the crystallization of anhydrite from the basaltic magma in the Kharaelakh intrusion, a logical assumption was that equilibrium between sulfate and sulfide would have been attained. However, ion microprobe analyses of coexisting sulfide minerals and anhydrite in the Kharaelakh intrusion indicate that isotopic equilibrium may be only locally achieved during subsolidus cooling. Our results have implications for the mechanisms of sulfur isotope exchange in high-temperature systems.

## 2. GEOLOGIC BACKGROUND

The Kharaelakh intrusion (previously known as the NW Talnakh intrusion) is one of several sills that host sulfide-rich Ni–Cu–(PGE) deposits in the Noril'sk region (Fig. 1). A detailed description of the rock types in the sill has been given by Czamanske et al. (1995). The ore-bearing intrusions tend to be flat, elongated bodies (15 × 2 × 0.2 km) that intruded Devonian argillites, evaporites, and coal deposits, as well as the lower part of a 3.5 km-thick volcanic sequence of basaltic lavas and tuffs associated with late Permian rifting. The ore deposits are commonly linked to the voluminous amount of plume-related magmatism which may have supplied metals, as well as to interaction with country rocks which provided additional sulfur. In addition to massive sulfide ores that occur in depressions near the bottom of the intrusion, picritic and taxitic gabbros that overlie the massive ore contain disseminated and droplet or globule sulfides with sulfide contents in the range of 3–20 vol.%. Our samples were taken from the disseminated/globule sulfide-bearing rock types.

There are two distinctive types of anhydrite that are readily identifiable in the examined samples. Gorbachev and Grinenko (1973) described "metasomatic" anhydrite in both the Kharaelakh intrusion and the contact aureole. In the samples that we have studied we equate their metasomatic anhydrite with a secondary hydrothermal anhydrite (Li et al., 2009a). This anhydrite cuts other rock types and is always associated with several secondary hydrothermal minerals including calcite, prehnite, pectolite, thomsonite, xonotlite, epidote, chlorite, hydrogrossular, and pyrite (e.g., Fig. 2). The prehnite–zeolite assemblage suggests temperatures of less than 400 °C (e.g., Liou et al., 1983; Leake, 1998), and we interpret the cross-cutting anhydrite to be part of a relatively low-temperature hydrothermal event. Patches of alteration minerals, including anhydrite, may locally reach 1 cm in diameter.

The second type of anhydrite is unrelated to the alteration minerals, and occurs interstitially to olivine, pyroxene, and plagioclase. The grain size of this type of anhydrite is generally less than 1 mm in diameter. Li et al. (2009a) have noted planar grain boundaries between anhydrite, olivine, and augite, and inclusions of anhydrite in augite and vice versa. We have examined polished thin sections of samples cut at a variety of orientations and the textural characteristics of anhydrite are identical in all orientations. For this reason we discard the possibility that this type of anhydrite represents remnant xenocrysts and instead interpret it to be a product of magmatic crystallization. Anhydrite may occur as a sole interstitial mineral (e.g., Fig. 3a), or may coexist with sulfide minerals and locally biotite. We stress that although both anhydrite and sulfide minerals may share an interstice (Fig. 3b), this is not a ubiquitous association and interstices filled with sulfides only also occur.

## 3. SAMPLING AND ANALYTICAL METHODS

Three of the samples (K46, K53, and K58) used in this study are from underground drill core P5536 which was collared in a drift in the Komsomolsky mine located in the eastern part of the Kharaelakh intrusion (Fig. 1). Sample KH-1 and KH-2 are from underground drill cores M685 and M690, respectfully, collared in stopes that are located in the western part of the intrusion (Fig. 1). Samples K46