

Titre du projet : Toward Improving the Thode's REaction (TITRE)

Volet : Recherche

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Laboratoires impliqués : IGE, LiPhy, IsTerre

Bilan du projet pour l'année/la période

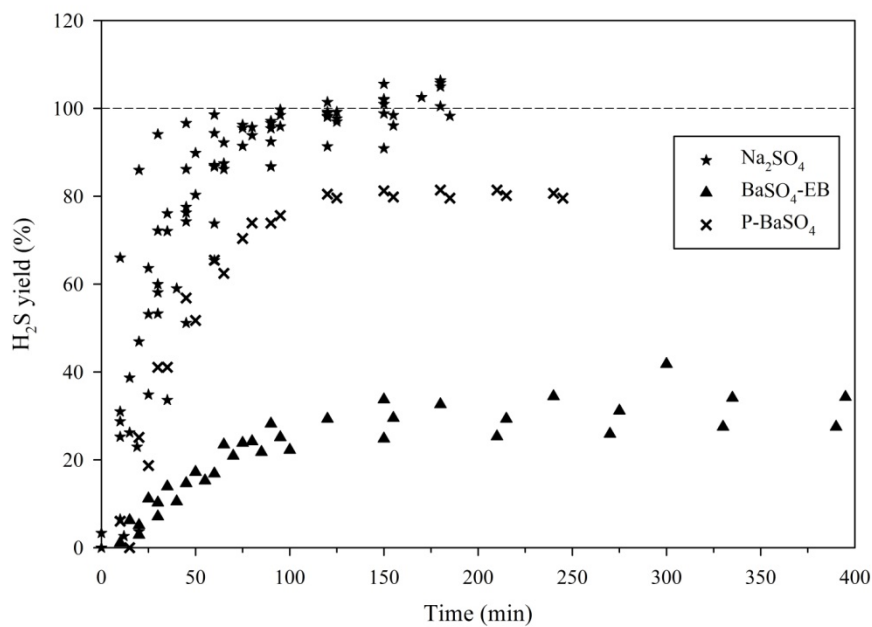
Bilan d'activité (1 page max)

The discovery of S-MIF (sulfur isotope mass-independent fractionation) provides a direct link between atmospheric composition and signals in the rock record and a new metric for the investigation of early Earth, as well as for the study of climate effect of volcanic eruptions. Precise analysis of four sulfur isotopes of sulfate in geological and environmental samples is necessary to access the magnitude of S-MIF, and thereby provides the means to extract unique information on atmospheric sulfur cycling as well as the chemical composition of ancient atmosphere. Reduction of sulfate to sulfide is the first step to access the four sulfur isotopes of sulfate samples. Currently many labs rely on a cumbersome distillation apparatus system and follow the use of what is called Thode's or Toba's reducing solution to reduce sulfate to sulfide. The method requires large volume of reducing solution (e.g., 30 ml), and each labs appear to have their own recipe on the exact composition of the reducing solution (e.g., H_3PO_3 vs. H_3PO_2 and/or different HI vs HCl ratio), and the procedure is not yet completely understood and reproducible between laboratories. A critical review of the literature suggests the key reagents for the reducing solution is HI and H_3PO_2 , and water should be avoided during the reaction. For the consideration of less water present, H_3PO_2 can be replaced with NaH_2PO_2 , and dry samples should be used. In order to test the new recipe, and to establish and run daily the conversion of sulfate to H_2S for batch treatment analysis in stopped vials, we need to follow the conversion yield of H_2S , which can be stabilized in a NaOH solution.

The UV/Vis spectrophotometer has been used intensely during the validation of the new method. The direct measurement of HS^- by UV absorption provides quick, and real-time assessment of the production of H_2S , which allows us not only obtain the time-resolved profile of the reaction, but also the precise time needed to reach a 100% reduction (Figure 1). The result demonstrate that our new protocol is reliable, time saver and more efficient in terms of reducing sulfate to sulfide. Based on this, we build a batch processing system that allows the reduction of multiple (8 or more) samples at a time, and the yield of H_2S can be accessed directly with the UV/Vis spectrophotometer, allowing a precise follow-up of chemistry from sulfate to sulfide which is impossible for the conventional method. We have a method paper written up on this and will be submitted soon.

The results benefited from the UV/Vis spectrophotometer have also been presented at many conferences, including Goldschmidt 2016 in Yokohama Japan, ISI 2016 in Nantes, France and Goldschmidt 2017, Paris, France.

Illustrations - avec légende et crédit (à envoyer également séparément)



Time-resolved yields of H₂S from the reduction of dry Na₂SO₄, BaSO₄-EB (BaSO₄ with excess Ba²⁺) and P-BaSO₄ (pure BaSO₄).

Production scientifique (articles scientifiques, actes de congrès...)

- Geng, L., Savarino, J., Hattori, S., Ishino, S., and Yoshida, N.: A new fluorination line for multiple sulfur isotope analysis, 26th Annual Goldschmidt Conference, Yokohama, Japan, 2016.
- Geng, L., Savarino, J., Hattori, S., and Ishino, S.: A new method of reducing sulfate to sulfide for multiple sulfur isotope analysis, 8th International Symposium on Isotopomers, Nantes, France, 2016.
- Geng, L., and Savarino, J.: Sulfur and oxygen isotopic signatures of sulfate aerosols produced in a large atmospheric simulation chamber, 27th Annual Goldschmidt Conference, Paris, France, 2017.
- Lei Geng, Joel Savarino, Clara Savarino, Nicolas Caillon, Pierre Cartigny, Shohei Hattori, Sakiko Ishino, Naohiro Yoshida, A simple and reliable method reducing sulfate to sulfide for multiple sulfur isotope analysis, Geol. Chem., soumis.
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Bilan financier succinct (avec suivant les cas : co-financements éventuels, équipements achetés, missions, recrutements divers, fonctionnements divers...)

Recettes

Dotation LabEx AO6 :	7 900 €
Marie Curie MISFIT/ANR FOFAMIF:	11 800 €

Dépenses

<u>Equipement</u> :	Spectrophotometre Jenway 6850 et accessoires :	7 500 €
<u>Fonctionnement</u> :	Flacons, fluides, swagelok, régulateur, etc.	7 000 €
<u>Missions</u> :	International Symposium on Isotopomers, Nantes 2016 :	400 €
	Goldschmidt 2016 – Yokohama :	2 000 €
	Goldschmidt 2017 – Paris :	1 300 €
<u>Frais publication:</u>	Geol Chem :	1 500 €



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N° total de cartons

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Ligne	Article N°	Désignation	Code UN	UOM	A expédier	Quantité expédiée	Quantité en reliquat
10	13236389	SPECTROPHOTOMETRE DOUBLE FAISCEAU 6850 Marque/Ref. Fabricant Jenway 6850/230V Pièce (EA) = 1 x 1,00 PCS Colis n° 351000000017496516		EA	1	1	

Article déjà expédié

20	13286389	TOURELLE AUTOMATIQUE 8 POSITIONS Date d'expédition: 16.06.16		EA		1	
40	11944385	X500 CUVE MACRO PMMA UV Date d'expédition: 10.05.16		EA		1	
50	11904385	X500 CUVE SEMIMICRO PMMA UV Date d'expédition: 10.05.16		EA		1	

Annexes si besoin ou lien sur des sites existants et pérennes jusqu'à la fin du Labex (2020)