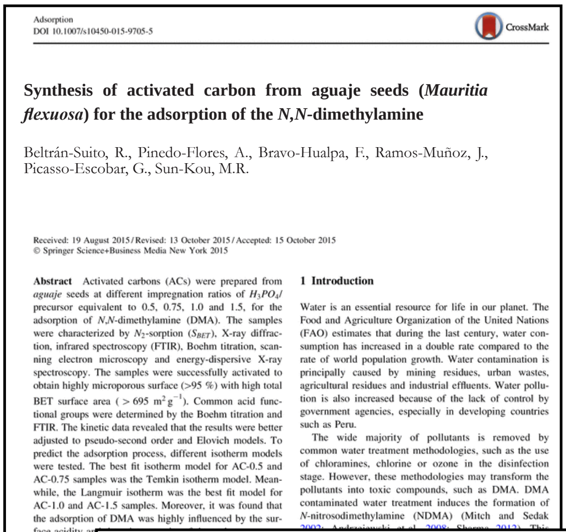
Artículos científicos (2015) de la Sección Química de la PUCP

Aquí encontrará la primera página y el link (solo accesible en el formato digital) de todos los artículos científicos publicados en revistas científicas internacionales por los integrantes de la Sección Química de la PUCP durante 2015.[*]



Adsorption
DOI 10.1007/s10450-015-9705-5

Synthesis of activated carbon from aguaje seeds (*Mauritia flexuosa*) for the adsorption of the *N,N*-dimethylamine

Beltrán-Suito, R., Pinedo-Flores, A., Bravo-Hualpa, F., Ramos-Muñoz, J., Picasso-Escobar, G., Sun-Kou, M.R.

Received: 19 August 2015 / Revised: 13 October 2015 / Accepted: 15 October 2015

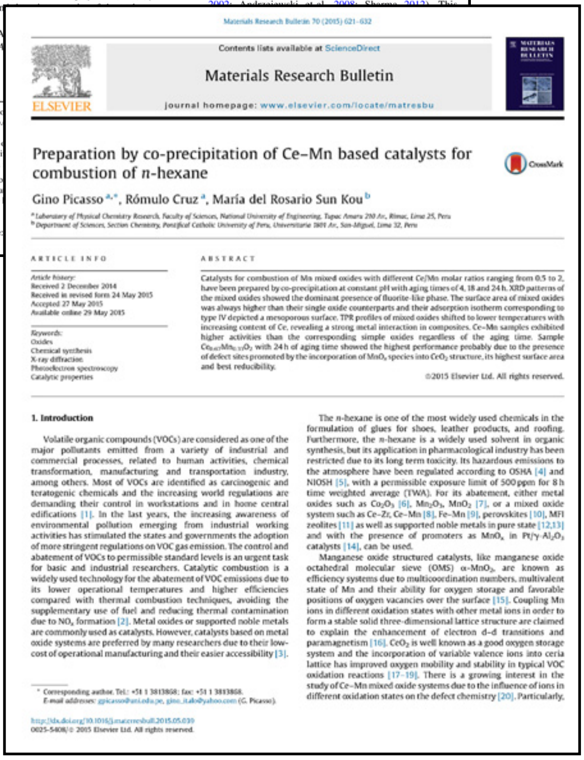
Abstract Activated carbons (ACs) were prepared from *aguaje* seeds at different impregnation ratios of H_3PO_4/precursor equivalent to 0.5, 0.75, 1.0 and 1.5, for the adsorption of *N,N*-dimethylamine (DMA). The samples were characterized by N_2-sorption (S_{BET}), X-ray diffraction, infrared spectroscopy (FTIR), Boehm titration, scanning electron microscopy and energy-dispersive X-ray spectroscopy. The samples were successfully activated to obtain highly microporous surface (>95 %) with high total BET surface area (> 695 $m^2 g^{-1}$). Common acid functional groups were determined by the Boehm titration and FTIR. The kinetic data revealed that the results were better adjusted to pseudo-second order and Elovich models. To predict the adsorption process, different isotherm models were tested. The best fit isotherm model for AC-0.5 and AC-0.75 samples was the Temkin isotherm model. Meanwhile, the Langmuir isotherm was the best fit model for AC-1.0 and AC-1.5 samples. Moreover, it was found that the adsorption of DMA was highly influenced by the surface acidity

1 Introduction

Water is an essential resource for life in our planet. The Food and Agriculture Organization of the United Nations (FAO) estimates that during the last century, water consumption has increased in a double rate compared to the rate of world population growth. Water contamination is principally caused by mining residues, urban wastes, agricultural residues and industrial effluents. Water pollution is also increased because of the lack of control by government agencies, especially in developing countries such as Peru.

The wide majority of pollutants is removed by common water treatment methodologies, such as the use of chloramines, chlorine or ozone in the disinfection stage. However, these methodologies may transform the pollutants into toxic compounds, such as DMA. DMA contaminated water treatment induces the formation of *N*-nitrosodimethylamine (NDMA) (Mitch and Sedak

---



Materials Research Bulletin 70 (2015) 621–632

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Preparation by co-precipitation of Ce–Mn based catalysts for combustion of *n*-hexane

Gino Picasso[a,*], Rómulo Cruz[a], María del Rosario Sun Kou[b]

[a] Laboratory of Physical Chemistry Research, Faculty of Sciences, National University of Engineering, Tupac Amaru 210 Av., Rimac, Lima 25, Peru
[b] Department of Sciences, Section Chemistry, Pontifical Catholic University of Peru, Universitaria 1801 Av., San-Miguel, Lima 32, Peru

ARTICLE INFO

Article history:
Received 2 December 2014
Received in revised form 24 May 2015
Accepted 27 May 2015
Available online 29 May 2015

Keywords:
Oxides
Chemical synthesis
X-ray diffraction
Photoelectron spectroscopy
Catalytic properties

ABSTRACT

Catalysts for combustion of Mn mixed oxides with different Ce/Mn molar ratios ranging from 0.5 to 2, have been prepared by co-precipitation at constant pH with aging times of 4, 18 and 24 h. XRD patterns of the mixed oxides showed the dominant presence of fluorite-like phase. The surface area of mixed oxides was always higher than their single oxide counterparts and their adsorption isotherm corresponding to type IV depicted a mesoporous surface. TPR profiles of mixed oxides shifted to lower temperatures with increasing content of Ce, revealing a strong metal interaction in composites. Ce–Mn samples exhibited higher activities than the corresponding simple oxides regardless of the aging time. Sample $Ce_{0.67}Mn_{0.33}O_2$ with 24 h of aging time showed the highest performance probably due to the presence of defect sites promoted by the incorporation of MnO_x species into CeO_2 structure, its highest surface area and best reducibility.

1. Introduction

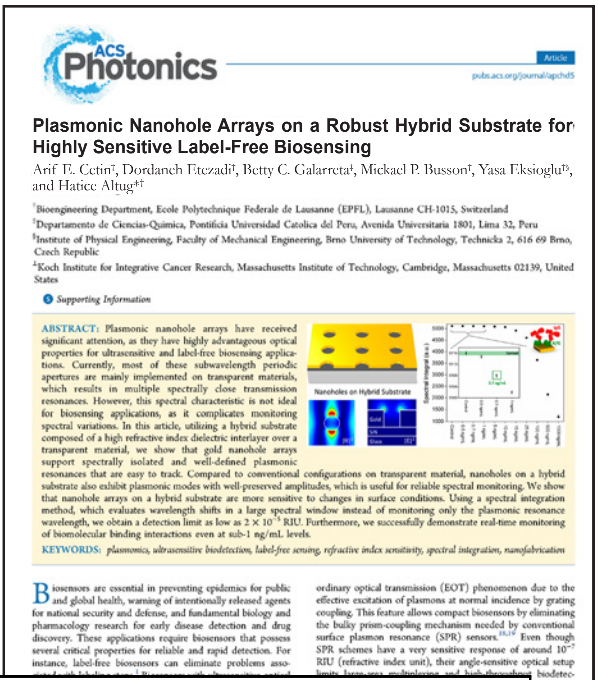
Volatile organic compounds (VOCs) are considered as one of the major pollutants emitted from a variety of industrial and commercial processes, related to human activities, chemical transformation, manufacturing and transportation industry, among others. Most of VOCs are identified as carcinogenic and teratogenic chemicals and the increasing world regulations are demanding their control in workstations and in home central edifications [1]. In the last years, the increasing awareness of environmental pollution emerging from industrial working activities has stimulated the states and governments the adoption of more stringent regulations on VOC gas emission. The control and abatement of VOCs to permissible standard levels is an urgent task for basic and industrial researchers. Catalytic combustion is a widely used technology for the abatement of VOC emissions due to its lower operational temperatures and higher efficiencies compared with thermal combustion techniques, avoiding the supplementary use of fuel and reducing thermal contamination due to NO_x formation [2]. Metal oxides or supported noble metals are commonly used as catalysts. However, catalysts based on metal oxide systems are preferred by many researchers due to their low-cost of operational manufacturing and their easier accessibility [3].

The *n*-hexane is one of the most widely used chemicals in the formulation of glues for shoes, leather products, and roofing. Furthermore, the *n*-hexane is a widely used solvent in organic synthesis, but its application in pharmacological industry has been restricted due to its long term toxicity. Its hazardous emissions to the atmosphere have been regulated according to OSHA [4] and NIOSH [5], with a permissible exposure limit of 500 ppm for 8 h time weighted average (TWA). For its abatement, either metal oxides such as Co_2O_3 [6], Mn_2O_3, MnO_2 [7], or a mixed oxide system such as Ce–Zr, Ce–Mn [8], Fe–Mn [9], perovskites [10], MFI zeolites [11] as well as supported noble metals in pure state [12,13] and with the presence of promoters as MnO_x in Pt/γ-Al_2O_3 catalysts [14], can be used.

Manganese oxide structured catalysts, like manganese oxide octahedral molecular sieve (OMS) α-MnO_2, are known as efficiency systems due to multicoordination numbers, multivalent state of Mn and their ability for oxygen storage and favorable positions of oxygen vacancies over the surface [15]. Coupling Mn ions in different oxidation states with other metal ions in order to form a stable solid three-dimensional lattice structure are claimed to explain the enhancement of electron d–d transitions and paramagnetism [16]. CeO_2 is well known as a good oxygen storage system and the incorporation of variable valence ions into ceria lattice has improved oxygen mobility and stability in typical VOC oxidation reactions [17–19]. There is a growing interest in the study of Ce–Mn mixed oxide systems due to the influence of ions in different oxidation states on the defect chemistry [20]. Particularly,

* Corresponding author. Tel.: +51 1 3813868; fax: +51 1 3813868.
E-mail addresses: gpicasso@uni.edu.pe, gino_italo@yahoo.com (G. Picasso).

http://dx.doi.org/10.1016/j.materresbull.2015.05.030



ACS Photonics
Article
pubs.acs.org/journal/apchd5

Plasmonic Nanohole Arrays on a Robust Hybrid Substrate for Highly Sensitive Label-Free Biosensing

Arif E. Cetin[†], Dordaneh Etezadi[†], Betty C. Galarreta[‡], Mickael P. Busson[†], Yasa Eksioglu[†§], and Hatice Altug*[†]

[†] Bioengineering Department, Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne CH-1015, Switzerland
[‡] Departamento de Ciencias-Quimica, Pontificia Universidad Catolica del Peru, Avenida Universitaria 1801, Lima 32, Peru
[§] Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Technicka 2, 616 69 Brno, Czech Republic
[⊥] Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: Plasmonic nanohole arrays have received significant attention, as they have highly advantageous optical properties for ultrasensitive and label-free biosensing applications. Currently, most of these subwavelength periodic apertures are mainly implemented on transparent materials, which results in multiple spectrally close transmission resonances. However, this spectral characteristic is not ideal for biosensing applications, as it complicates monitoring spectral variations. In this article, utilizing a hybrid substrate composed of a high refractive index dielectric interlayer over a transparent material, we show that gold nanohole arrays support spectrally isolated and well-defined plasmonic resonances that are easy to track. Compared to conventional configurations on transparent material, nanoholes on a hybrid substrate also exhibit plasmonic modes with well-preserved amplitudes, which is useful for reliable spectral monitoring. We show that nanohole arrays on a hybrid substrate are more sensitive to changes in surface conditions. Using a spectral integration method, which evaluates wavelength shifts in a large spectral window instead of monitoring only the plasmonic resonance wavelength, we obtain a detection limit as low as 2 × 10^{-5} RIU. Furthermore, we successfully demonstrate real-time monitoring of biomolecular binding interactions even at sub-1 ng/mL levels.

KEYWORDS: *plasmonics, ultrasensitive biodetection, label-free sensing, refractive index sensitivity, spectral integration, nanofabrication*

Biosensors are essential in preventing epidemics for public and global health, warning of intentionally released agents for national security and defense, and fundamental biology and pharmacology research for early disease detection and drug discovery. These applications require biosensors that possess several critical properties for reliable and rapid detection. For instance, label-free biosensors can eliminate problems asso-

ordinary optical transmission (EOT) phenomenon due to the effective excitation of plasmons at normal incidence by grating coupling. This feature allows compact biosensors by eliminating the bulky prism-coupling mechanism needed by conventional surface plasmon resonance (SPR) sensors.[18,19] Even though SPR schemes have a very sensitive response of around 10^{-7} RIU (refractive index unit), their angle-sensitive optical setup

---

98 Gant et al.: Journal of AOAC International Vol. 98, No. 1, 2015

FOOD COMPOSITION AND ADDITIVES

Validated HPLC-Diode Array Detector Method for Simultaneous Evaluation of Six Quality Markers in Coffee

ANASTASIA GANT, VANESSA E. LEYVA , ANA E. GONZALEZ, AND HELENA MARUENDA[1]
Pontificia Universidad Catolica del Peru (PUCP), Departamento de Ciencias–Quimica, Av. Universitaria 1801, Lima 32, Peru

Nicotinic acid, *N*-methylpyridinium ion, and trigonelline are well studied nutritional biomarkers present in coffee, and they are indicators of thermal decomposition during roasting. However, no method is yet available for their simultaneous determination. This paper describes a rapid and validated HPLC-diode array detector method for the simultaneous quantitation of caffeine, trigonelline, nicotinic acid, *N*-methylpyridinium ion, 5-caffeoylquinic acid, and 5-hydroxymethyl furfural that is applicable to three coffee matrixes: green, roasted, and instant. Baseline separation among all compounds was achieved in 30 min using a phenyl-hexyl RP column (250 × 4.6 mm, 5 µm particle size), 0.3% aqueous formic buffer (pH 2.4)–methanol mobile phase at a flow rate of 1 mL/min, and a column temperature at 30°C. The method showed good linear correlation (r^2 > 0.9985), precision (less than 3.9%), sensitivity (LOD = 0.023–0.237 µg/mL; LOQ = 0.069–0.711 µg/mL), and recovery (84–102%) for all compounds. This simplified method is amenable for a more complete routine evaluation of coffee in industry.

Coffee is one of the most consumed beverages in the world. Its quality is typically evaluated by professional cuppers trained to assess subjective contributors to flavor and aroma. Quality may also be monitored via a more objective evaluation, particularly through the content of compounds known as coffee taste descriptors, namely, caffeine (**1**), trigonelline (**2**), nicotinic acid (**3**), *N*-methylpyridinium ion (**4**), 5-monocaffeoylquinic acid (5-CQA) (**5**), and 5-hydroxymethyl furfural (**6**) (1–4).

coffee roasting markers a difficult task. The quantitation of **4**, a compound not retained on RP columns, requires a separate analytical method based on ion-exchange chromatography (10). Recently, nonconventional HPLC methods, which include the use of two columns of different stationary phases connected in series (11) or hydrophilic interaction liquid chromatography coupled to MS (12), have been implemented in order to improve resolution between **2** and **3** (11) and **2** and **4** (12).

The herein proposed RP-HPLC-DAD method allowed baseline separation and quantitation of quality markers **1–6** in 30 min. The method has been validated for green, roasted, and instant coffee matrixes. The identities of **1–6** in coffee were confirmed by LC/MS/MS.

Experimental

Chemicals and Coffee Samples

All standard compounds were purchased from Sigma-Aldrich (St. Louis, MO). *N*-methylpyridinium iodide and **6** were synthesized and fully characterized by NMR spectrometry and electrospray ionization (ESI)/MS analysis following the available literature procedures (13–15). Methanol (MeOH; HPLC grade) was purchased from J.T. Baker (Griesheim, Germany), and the water for HPLC-DAD and LC/MS analyses was MilliQ purified (EMD Millipore Corp., Billerica, MA).

Green specialty coffee (*Coffea arabica*) was obtained from Jaen-Cajamarca, Peru. The coffee was roasted by professionals from CENFROCAFE (Cooperativa de Servicios Multiples, Peru). The instant coffee sample was purchased from a commercial

---

Research
New Phytologist

Global variability in leaf respiration in relation to climate, plant functional types and leaf traits.

Owen K. Atkin[1,2], Keith J. Bloomfield[2], Peter B. Reich[3,4], Mark G. Tjoelker[4], Gregory P. Asner[5], Damien Bonal[6], Gerhard Bönisch[7], Matt G. Bradford[8], Lucas A. Cernusak[9], Eric G. Cosio[10], Danielle Creek[2,4], Kristine Y. Crous[2,4], Tomas F. Domingues[11], Jeffrey S. Dukes[12,13], John J. G. Egerton[2], John R. Evans[2], Graham D. Farquhar[2], Nikolaos M. Fyllas[14], Paul P. G. Gauthier[2,15], Emanuel Gloor[16], Teresa E. Gimeno[4], Kevin L. Griffin[17], Rossella Guerrieri[18,19], Mary A. Heskel[2], Chris Huntingford[20], Françoise Yoko Ishida[9], Jens Kattge[7], Hans Lambers[21], Michael J. Liddell[22], Jon Lloyd[9,23], Christopher H. Lusk[24], Roberta E. Martin[5], Ayal P. Maksimov[25], Trofim C. Maximov[25], Yadvinder Malhi[26], Belinda E. Medlyn[27,4], Patrick Meir[2,18], Lina M. Mercado[28,20], Nicholas Mirotchnick[29], Desmond Ng[2,30], Ülo Niinemets[31], Odhran S. O'Sullivan[2], Oliver L. Phillips[16], Lourens Poorter[32], Pieter Poot[21], I. Colin Prentice[27,23], Norma Salinas[10,26], Lucy M. Rowland[18], Michael G. Ryan[33], Stephen Sitch[28], Martijn Slot[34,35], Nicholas G. Smith[13], Matthew H. Turnbull[36], Mark C. VanderWel[34,37], Fernando Valladares[38], Erik J. Veneklaas[21], Lasantha K. Weerasinghe[2,39], Christian Wirth[40], Ian J. Wright[27], Kirk R. Wythers[3], Jen Xiang[1,2], Shuang Xiang[2,41] and Joana Zaragoza-Castells[18,28]

Author for correspondence:
Owen K. Atkin
Tel +61 0 2 6125 5046
Email: Owen.Atkin@anu.edu.au

Summary

- Leaf dark respiration (R_{dark}) is an important yet poorly quantified component of the global carbon cycle. Given this, we analyzed a new global database of R_{dark} and associated leaf traits.

614 *New Phytologist* (2015) 206: 614–636
www.newphytologist.com

---

[*] Solo se incluyen artículos de los integrantes de la Sección Química de la PUCP que aparezcan firmados con la afiliación a esta Sección, independientemente de si los colaboradores son, o no, de la PUCP. El acceso al artículo depende de la suscripción del usuario a las editoriales correspondientes. Se han incluido solo revistas científicas que se encuentran indexadas en las bases de datos **Scopus** y **Web of Science**, de reconocido prestigio internacional.

Phytochemistry 116 (2015) 138–148

Contents lists available at ScienceDirect

Phytochemistry

journal homepage: www.elsevier.com/locate/phytochem

Bioactive Maca (*Lepidium meyenii*) alkamides are a result of traditional Andean postharvest drying practices

Eliana Esparza[a], Antonella Hadzich[a], Waltraud Kofer[a], Axel Mithöfer[b], Eric G. Cosio[a]

[a] Sección Química, Pontificia Universidad Católica del Perú, Avenida Universitaria 1801, San Miguel, Lima 32, Peru
[b] Department of Bioorganic Chemistry, Max Planck Institute for Chemical Ecology, Hans-Knöll-Straße 8, 07745 Jena, Germany

ARTICLE INFO

Article history:
Received 30 June 2014
Received in revised form 9 February 2015
Available online 25 March 2015

Keywords:
Maca
Lepidium meyenii
Brassicaceae
Post-harvest processing
Alkamides
Macamides
Glucosinolates
Benzylamine
Benzylisothiocyanate
Fatty acid amide hydrolase

ABSTRACT

Maca, *Lepidium meyenii* Walpers (Brassicaceae), is an annual herbaceous plant native to the high plateaus of the Peruvian central Andes. Its underground storage hypocotyls have been a traditional medicinal agent and dietary staple since pre-Columbian times. Reported properties include energizing and fertility-enhancing effects. Published reports have focused on the benzylalkamides (macamides) present in dry hypocotyls as one of the main bioactive components. Macamides are secondary amides formed by benzylamine and a fatty acid moiety, with varying hydrocarbon chain lengths and degree of unsaturation. Although it has been assumed that they are usually present in fresh undamaged tissues, analyses show them to be essentially absent from them. However, hypocotyls dried by traditional Andean postharvest practices or industrial oven drying contain up to 800 μg g^{-1} dry wt (2.3 μmol g^{-1} dry wt) of macamides. In this study, the generation of macamides and their putative precursors were studied during nine-week traditional drying trials at 4200 m altitude and in ovens under laboratory conditions. Freeze–thaw cycles in the open field during drying result in tissue maceration and release of free fatty acids from storage and membrane lipids up to levels of 1200 μg g^{-1} dry wt (4.3 μmol g^{-1} dry wt). Endogenous metabolism of the isothiocyanates generated from glucosinolate hydrolysis during drying results in maximal benzylamine values of 4300 μg g^{-1} dry wt (40.2 μmol g^{-1} dry wt). Pearson correlation coefficients of the accumulation profiles of benzylamine and free fatty acid to that of macamides showed good values of 0.898 and 0.934, respectively, suggesting that both provide sufficient substrate for amide synthesis during the drying process.

1. Introduction

Maca (*Lepidium meyenii* Walpers or *Lepidium peruvianum* Chacón), an annual herbaceous plant of the Brassicaceae family, is native to the central Andes. It is the only reported species of the genus *Lepidium* displaying a fused hypocotyl and taproot forming an underground storage

Maca presents three major phenotypes, red, yellow and black (Fig. 1), based on their hypocotyl and stem coloration. As in most Brassicaceae, glucosinolates accumulate in its tissues, of which benzylglucosinolate (**1**) (Fig. 2) is the main product. Depending on the chemotype, lesser amounts of the 3- or 4-, hydroxy or methoxylated benzyl derivatives (**14–17**) (Fig. S1) and of trypto-

---

nature climate change LETTERS

PUBLISHED ONLINE: 2 MARCH 2015 | DOI: 10.1038/NCLIMATE2550

Optimal stomatal behaviour around the world

Yan-Shih Lin *et al.*†

Stomatal conductance (g_s) is a key land-surface attribute as it links transpiration, the dominant component of global land evapotranspiration, and photosynthesis, the driving force of the global carbon cycle. Despite the pivotal role of g_s in predictions of global water and carbon cycle changes, a global-scale database and an associated globally applicable model of g_s that allow predictions of stomatal behaviour are lacking. Here, we present a database of globally distributed g_s obtained in the field for a wide range of plant functional types (PFTs) and biomes. We find that stomatal behaviour differs among PFTs according to their marginal carbon cost of water use, as predicted by the theory underpinning the optimal stomatal model[1] and the leaf and wood economics spectrum[2,3]. We also demonstrate a global relationship with climate. These findings provide a robust theoretical framework for understanding and predicting the behaviour of g_s across biomes and across PFTs that can be applied to regional, continental and global-scale modelling of ecosystem productivity, energy balance and ecohydrological processes in a future changing climate.

Earth system models (ESMs), which integrate biogeochemical and biogeophysical land-surface processes with physical climate models, have been widely used to demonstrate the importance of land-surface processes in determining climate and to highlight the large uncertainties in quantifying land-surface processes[4–6]. Within the biogeophysical components of land-surface processes, g_s plays a pivotal role because it is a key feedback route for carbon and water exchange between the atmosphere and terrestrial vegetation. Stomata are small pores on leaves whose aperture is actively regulated by plants in response to multiple abiotic and biotic factors, and their conductance is a major determinant of global land evapotranspiration and global water and carbon cycles. Therefore, our ability to model the global carbon and water cycles under a future changing climate depends on our ability to predict g_s globally[7]. Many ESMs at present use an empirical stomatal model to predict g_s and, in the absence of information, assume identical parameter values for all non-water-stressed C_3 and C_4 vegetation. For example, the LPJ model[8] assumes a constant ratio of intercellular to ambient CO_2 concentration (C_i:C_a) of 0.8 for all C_3 vegetation and 0.4 for all C_4 vegetation. The CABLE model[9] uses the empirical

Figure 1 | Climatic space covered by the Stomatal Behaviour Synthesis Database, shown as mean temperature during the period with daily mean temperatures above 0 °C and moisture index. Coloured circles represent climatic space for the database, with different colours indicating different plant functional types. Grey hexagons represent global climatic space for which vegetation is present. The global climatic space data were binned by every 1 °C for temperatures above 0 °C ($\bar{T}$) and every 0.25 for the moisture index (MI). The grey scale bar indicates the number of 0.5 × 0.5 degree pixels for a given binned $\bar{T}$ and MI combination.

underlying this model[1] is that stomata are regulated so as to maximize photosynthesis minus the carbon cost of transpiration, $A-\lambda E$, where λ (mol CO_2 mol^{-1} H_2O) is the carbon cost per unit water used by the plant. Intuitively, λ represents the plant's exchange rate between carbon uptake and water use: a high value of λ indicates that transpiration is costly in carbon terms, meaning that the plant is likely to be conservative in its use of water. From this premise, the model predicts that g_s should be related to photosynthesis, vapour pressure deficit and atmospheric CO_2 concentration, with a single slope parameter, g_1, that is inversely proportional to $\sqrt{\lambda}$ (refs 1,14,15). The slope parameter g_1 is readily estimated from experimental data (Methods) and can be used as an index of λ, where small values of g_1 indicate a high λ. The model also

---

Biogeosciences, 12, 6071–6083, 2015
www.biogeosciences.net/12/6071/2015/
doi:10.5194/bg-12-6071-2015

Soil microbial nutrient constraints along a tropical forest elevation gradient: A belowground test of a biogeochemical paradigm

A. T. Nottingham[1], B. L. Turner[2], J. Whitaker[3], N. J. Ostle[4], N. P. McNamara[3], R. D. Bardgett[5], N. Salinas[6,7,8], and P. Meir[1,9]

[1] School of Geosciences, University of Edinburgh, Drummond Street, Edinburgh, EH8 9XP, UK
[2] Smithsonian Tropical Research Institute, Apartado 0843-03092, Balboa, Ancon, Republic of Panama
[3] Centre for Ecology & Hydrology, Lancaster Environment Centre, Library Avenue, Lancaster, LA1 4AP, UK
[4] Lancaster Environment Centre, Lancaster University, Bailrigg, Lancaster, LA1 4YQ, UK
[5] Faculty of Life Sciences, Michael Smith Building, The University of Manchester, Oxford Road, Manchester, M13 9PT, UK
[6] Seccion Química, Pontificia Universidad Católica del Peru, Lima, Peru
[7] Universidad Nacional de San Antonio Abad del Cusco, Facultad de Biologia, Cusco, Peru
[8] Environmental Change Institute, School of Geography and the Environment, South Parks Road, Oxford, OX1 3QY, UK
[9] Research School of Biology, Australian National University, Canberra, ACT 0200, Australia

Correspondence to: A. T. Nottingham (anotting@staffmail.ed.ac.uk)

Received: 26 February 2015 – Published in Biogeosciences Discuss.: 30 April 2015
Revised: 19 August 2015 – Accepted: 19 August 2015 – Published: 26 October 2015

Abstract. Aboveground primary productivity is widely considered to be limited by phosphorus (P) availability in lowland tropical forests and by nitrogen (N) availability in montane tropical forests. However, the extent to which this paradigm applies to belowground processes remains unresolved. We measured indices of soil microbial nutrient status in lowland, sub-montane and montane tropical forests along a natural gradient spanning 3400 m in elevation in the Peruvian Andes. With increasing elevation there were marked increases in soil concentrations of total N, total P, and readily exchangeable P, but a decrease in N mineralization determined by in situ resin bags. Microbial carbon (C) and N increased with increasing elevation, but microbial C : N : P ratios were relatively constant, suggesting homeostasis. The activity of hydrolytic enzymes, which are rich in N, decreased with increasing elevation, while the ratio of enzymes involved in the acquisition of N and P increased with increasing elevation, further indicating an increase in the relative demand for N compared to P with increasing elevation. We conclude that soil microorganisms shift investment in nutrient

1 Introduction

Tropical forests have a major influence on the global carbon (C) cycle, being the most productive ecosystems on Earth and containing 34–55 % of the C in forests worldwide (Beer et al., 2010; Pan et al., 2011). The exchange of C between the atmosphere and forests is mediated by the availability of mineral nutrients, so there is widespread interest in understanding how plant or microbial metabolic processes are constrained by the deficiencies of specific "limiting" nutrients (Cleveland et al., 2011; Wright et al., 2011), and how human alteration of these nutrient cycles may impact tropical ecosystems (Hietz et al., 2011; Townsend et al., 2011). Our understanding of nutrient limitation in the tropical forest C cycle is based largely on the responses of aboveground production. In contrast, belowground processes remain relatively under-studied, despite evidence that they are limited by different nutrients to those limiting aboveground productivity in some ecosystems, including tropical forests (Sun-

---

Special Section on Tropical Forests

Climate Warming and Soil Carbon in Tropical Forests: Insights from an Elevation Gradient in the Peruvian Andes

ANDREW T. NOTTINGHAM, JEANETTE WHITAKER, BENJAMIN L. TURNER, NORMA SALINAS, MICHAEL ZIMMERMANN, YADVINDER MALHI AND PATRICK MEIR

The temperature sensitivity of soil organic matter (SOM) decomposition in tropical forests will influence future climate. Studies of a 3.5-kilometer elevation gradient in the Peruvian Andes, including short-term translocation experiments and the examination of the long-term adaptation of biota to local thermal and edaphic conditions, have revealed several factors that may regulate this sensitivity. Collectively this work suggests that, in the absence of a moisture constraint, the temperature sensitivity of decomposition is regulated by the chemical composition of plant debris (litter) and both the physical and chemical composition of preexisting SOM: higher temperature sensitivities are found in litter or SOM that is more chemically complex and in SOM that is less occluded within aggregates. In addition, the temperature sensitivity of SOM in tropical montane forests may be larger than previously recognized because of the presence of "cold-adapted" and nitrogen-limited microbial decomposers and the possible future alterations in plant and microbial communities associated with warming. Studies along elevation transects, such as those reviewed here, can reveal factors that will regulate the temperature sensitivity of SOM. They can also complement and guide in situ soil-warming experiments, which will be needed to understand how this vulnerability to temperature may be mediated by altered plant productivity under future climatic change.

Keywords: decomposition, temperature sensitivity, tropical lowland forest, tropical montane forest, soil microorganisms, soil organic matter

The response of soil carbon to future temperature change will influence atmospheric composition and climate (Davidson and Janssens 2006, Conant et al. 2011), but the direction and magnitude of the resulting climate feedback remain unclear (IPCC 2013, Wieder et al. 2013). This is especially so for tropical forests, which constitute a disproportionately large component of the global carbon cycle, exchanging more carbon dioxide (CO_2) with the atmosphere than any other ecosystem and accounting for over two-thirds of terrestrial plant biomass (Pan et al. 2011) and a third of global soil carbon (Jobbagy and Jackson 2000). But the future carbon cycle of tropical forests, for which *in situ* temperature manipulation experiments have not been conducted (Cavaleri et al. 2015), remains an important source of uncertainty in climate model projections (Cox et al. 2013).

The tropics are predicted to experience novel heat regimes with a warming of 1.8 to 5.0 degrees Celsius (°C) over this century, resulting

closed canopy forest exists today (Wright et al. 2009, IPCC 2013). Earth system models currently predict that this warming will increase microbial mineralization of stable soil organic matter (SOM), resulting in a net release of carbon from soil into the atmosphere (Davidson and Janssens 2006, Wieder et al. 2013). Even a small fractional release of total soil carbon will have a significant impact on the concentration of atmospheric CO_2, because carbon storage in soils is three times greater than in the atmosphere and four times greater than in vegetation (Jobbagy and Jackson 2000).

Predictions about the future of tropical soil carbon remain uncertain, not only because no soil-warming experiments have been conducted in tropical forests (Cavaleri et al. 2015), but also because we still lack a general understanding of the complex direct and indirect factors that determine the long-term sensitivity of soil-carbon loss under elevated temperature. Short-term soil-warming experiments have

---

Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2015, **44**, 13716

Structural phase transitions and magnetic and spectroscopic properties of the double perovskites $Sr_2Co_{1-x}Mg_xTeO_6$ (x = 0.1, 0.2 and 0.5)

B. Orayech,[*a] L. Ortega-San-Martín,[b] I. Urcelay-Olabarria,[ac] L. Lezama,[cd] T. Rojo,[e] María I. Arriortua[f] and J. M. Igartua[g]

Received 28th May 2015,
Accepted 17th June 2015

DOI: 10.1039/c5dt02026c

www.rsc.org/dalton

The structural and magnetic properties of a series of ordered double perovskites with the formula $Sr_2Co_{1-x}Mg_xTeO_6$ (x = 0.1, 0.2 and 0.5) are investigated by X-ray diffraction, low temperature neutron diffraction, electron paramagnetic resonance and magnetic susceptibility. The progressive substitution of the paramagnetic Co^{2+} high spin ion by the diamagnetic Mg^{2+}, of about the same size, induces changes in the room temperature crystal structure, from a distorted $P2_1/n$ phase for the undoped Sr_2CoTeO_6 oxide to the $I4/m$ of the end member (Sr_2MgTeO_6). These perovskites experience structural transitions on heating, the temperature at which the transitions occur being smaller as x increases. The novel approach of mode-crystallography is used for the analysis. All oxides show antiferromagnetic exchange interactions between Co^{2+} ions but the long range antiferromagnetic order is not achieved for the phase with x = 0.5. The low temperature neutron diffraction data have been evaluated using a full symmetry analysis. Results are consistent with an unquenched orbital contribution of a high spin Co^{2+} ion.

1. Introduction

Double perovskites of the general formula $A_2BB'O_6$ (with A typically being an alkaline earth, B a low oxidation state transition metal and B' a small and highly charged ion) in which the B and B' ions are completely ordered in the structure are still of great interest. The possibility of different degrees of cation order in these oxides allows for the development of different properties that arise from the coupling of spin, charge and orbital degrees of freedom of the transition metal ions. Oxides of this type have received much attention in recent years due to the observation of properties with high application potential such as the large magnetoresistance and room temperature half metallicity observed in Sr_2FeMoO_6 and related oxides,[1,2] high ionic conductivity in $Sr_2Mg_{1-x}Mn_xMoO_{6-\delta}$[3] or the coexistence of ferroelectricity and ferromagnetism (multiferroic behavior) in Bi_2NiMnO_6[4] and La_2NiMnO_6.[5] More recently, some double perovskites have even been used as host materials for light emitting Eu^{3+} phosphors with promising results,[6] demonstrating that the double perovskite structure still holds interesting properties if appropriate elements are introduced into the lattice.

The study of cobalt containing double perovskites with the formula $A_2CoB'O_6$ has gained interest in recent years. $Ba_2CoMo_{0.5}Nb_{0.5}O_{6-\delta}$, with a mixed Co^{2+}/Co^{3+} oxidation state, for example, was proposed as a potential Solid Oxide Fuel Cell (SOFC) cathode,[7] whereas $La_{2-x}Sr_xCoTiO_6$ oxides have shown promising results both as cathode and anode electrodes for SOFCs.[8] The oxides with the formula A_2CoTeO_6 (A = Sr, Pb, Ca, Ba and Cd) have shown, on the other hand, that their magnetic behavior does not follow the one observed in similar compounds with B' cations different from Te^{6+}.[9] The latter compounds show interesting structural changes when the A-site cation is changed (from conventional perovskite phases if A is small to hexagonal modifications if it is very large as in the case of Ba^{2+} ions[10]) and also when the temperature is changed (if A = Sr[11] or Pb,[12] so far). The latter compounds, despite the differences in their structure, always show antiferromagnetic behavior due to the super-exchange interactions between Co^{2+} ions.

---

[a] Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, P.O. Box 644, Bilbao 48080, Spain. E-mail: brahim.orayech@ehu.es
[b] Departamento de Ciencias, Sección Química, Pontificia Universidad Católica del Perú (PUCP), Av. Universitaria 1801, Lima-32, Peru
[c] BCMaterials, Technological Park of Biscay, 48160 Derio, Spain
[d] Departamento de Química Inorgánica, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain
[e] CICenergigune, Albert Einstein 48, 01510 Miñano, Álava, Spain
[f] Universidad del País Vasco/Euskal Herriko Unibertsitatea (UPV/EHU), Facultad de Ciencia y Tecnología, Dpto. Mineralogía y Petrología, B. Sarriena s/n, 48940 Leioa (Vizcaya), Spain
[g] Fisika Aplikatua II Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, P.O. Box 644, Bilbao 48080, Spain

13716 | *Dalton Trans.*, 2015, **44**, 13716–13724

Directional solidification, thermo-mechanical and optical properties of $(Mg_xCa_{1-x})_3Al_2Si_3O_{12}$ glasses doped with Nd^{3+} ions

D. Sola,[1,*] D. Conejos,[1] J. Martínez de Mendivil,[2] L. Ortega-San-Martín,[3] G. Lifante,[2] and J.I. Peña[1]

[1] Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, Departamento de Ciencia y Tecnología de Materiales y Fluidos, C/ María de Luna 3, 50.018 Zaragoza, Spain
[2] Departamento de Física de Materiales, C-04, Facultad de Ciencias, Universidad, Autónoma de Madrid, Avda. Tomás y Valiente 7, 28.049 Madrid, Spain
[3] Departamento Sección Química, Pontificia Universidad Católica del Perú, Av. Universitaria 1801, San Miguel, Lima 32, Perú
**dsola@unizar.es*

Abstract: In this work glass rods of $(Mg_xCa_{1-x})_3Al_2Si_3O_{12}$ (x = 0, 0.5 and 1) doped with 1 wt% Nd_2O_3 were produced by the laser floating zone technique. Thermo-mechanical and spectroscopic properties have been evaluated. The three glass samples present good thermo-mechanical properties, with similar hardness, toughness and glass transition temperatures. The spectroscopic characterization shows spectral shifts in absorption and emission spectra. These spectral shifts together with Judd-Ofelt intensity parameters and ionic packing ratio have been used to investigate the local structure surrounding the Nd^{3+} ions and the covalency of the Nd-O bond. All obtained results agree and confirm the higher covalency of the Nd-O bond in the $Ca_3Al_2Si_3O_{12}$ glass.

OCIS codes: (160.5690) Rare-earth-doped materials; (300.6360) Spectroscopy, laser; (160.2750) Glass and other amorphous materials.

References and links

1. K. Hirao, T. Mitsuyu, J. Si, and J. Qiu, *Active Glass for Photonic Devices: Photoinduced Structures and their Application* (Springer-Verlag, 2001).
2. J. H. Campbel, J. S. Hayden, and A. J. Marker, "High-power solid-state lasers from a laser glass perspective," Int. J. Appl. Glass Sci. **2**(1), 3–29 (2011).
3. E. Snitzer, "Optical maser action of Nd^{+3} in a barium crown glass," Phys. Rev. Lett. 7(12), 444–446 (1961).
4. E. M. Erbe and D. E. Day, "Properties of Sm_2O_3-Al_2O_3-SiO_2 glasses for in vivo applications," J. Am. Ceram. Soc. 7**3**(9), 2708–2713 (1990).
5. E. V. Uhlmann, M. C. Weinberg, N. J. Kreidl, L. L. Burgner, R. Zanoni, and K. H. Church, "Spectroscopic properties of rare-earth-doped calcium-aluminate-based glasses," J. Non-Cryst. Solids **178**, 15–22 (1994).
6. S. L. Lin and C. S. Hwang, "Structures of CeO_2-Al_2O_3-SiO_2 glasses," J. Non-Cryst. Solids **202**(1-2), 61–67 (1996).
7. M. L. Baesso, A. C. Bento, L. C. M. Miranda, D. F. de Souza, J. A. Sampaio, and L. A. O. Nunes, "Rare-earth doped low silica calcium aluminosilicate glasses for near and mid infrared applications," J. Non-Cryst. Solids **276**(1-3), 8–18 (2000).
8. J. Marchi, D. S. Morais, J. Schneider, J. C. Bressiani, and A. H. A. Bressiani, "Characterization of rare earth aluminosilicate glasses," J. Non-Cryst. Solids **351**(10-11), 863–868 (2005).
9. A. Steimacher, M. J. Barboza, A. M. Farias, O. A. Sakai, J. H. Rohling, A. C. Bento, M. L. Baesso, A. N. Medina, and C. M. Lepienski, "Preparation of Nd_2O_3-doped calcium aluminosilicate glasses and thermo-optical and mechanical characterization," J. Non-Cryst. Solids **354**(42-44), 4749–4754 (2008).
10. L. Mota, J. A. Sampaio, M. G. da Silva, and H. Vargas, "Assessment of nonradiative relaxation time and characteristic diffusion time of neodymium, erbium and cobalt doped low silica calcium aluminosilicate glasses," Chem. Phys. Lett. **502**(1-3), 69–71 (2011).
11. A. Prnova, A. Domanicka, R. Klement, J. Kraxner, M. Polovka, M. Pentrak, D. Galusek, P. Simurka, and J. Kozankova, "Er- and Nd-doped yttrium aluminosilicate glasses: preparation and characterization," Opt. Mater. **33**(12), 1872–1878 (2011).

#239926 Received 29 Apr 2015; revised 15 Jun 2015; accepted 16 Jun 2015; published 30 Sep 2015
© 2015 OSA 5 Oct 2015 | Vol. 23, No. 20 | DOI:10.1364/OE.23.026356 | OPTICS EXPRESS 26356

Corrected: 21 October 2015