

## NICE DAY OUT FOR A MATERIALS SCIENTIST

A recent visit to the Isle of Mull, off western Scotland (*Elements* 6: 198), took me to the type localities of three minerals, mullite, tobermorite and kilchoanite. All three are rare in Nature but two are of enormous importance in the materials science world. Mullite is a close relative of sillimanite but with variable stoichiometry,  $Al_{4+2x}Si_{2-2x}O_{10-x}$ , where  $x$  is  $\sim 0.2-0.6$ . It was first identified in 1924, during experimental work on the system  $Al_2O_3-SiO_2$  by N.L. Bowen and J.W. Greig (no less) at the Geophysical Lab, on the  $3Al_2O_3 \cdot 2SiO_2$  composition. They considered it would occur naturally and obtained samples of glassy buchites, formed by fusion of argillaceous xenoliths in basaltic sills, from Seabank Villa on Mull<sup>1</sup>. They found needles of their new phase embedded in glass and were able to separate them by dissolving the glass overnight in cold HF. The name 'mullite' was proposed by Bowen, Greig and E.G. Zeis in the same year.

Mullite is an extremely widely employed refractory substance with a melting point of up to 1830 °C, depending on composition. Typing 'mullite' into Web of Science raised 4163 papers, currently receiving nearly 3500 citations per year. The people of the Hesse region of Germany unwittingly established its use in high-temperature ceramics in the 15<sup>th</sup> century when they developed a way of making refractory crucibles by heating mixtures of very pure kaolinite and quartz to >1100 °C, essentially the reaction studied by Bowen and his colleagues 500 years later. 'Hessian crucibles' were much in demand by early alchemists and were traded all over Europe, even reaching the distant colony in Virginia. Today mullite has many high-tech uses, including optical systems and linings in aircraft engines and on the surfaces of space vehicles. Sintered, mullite-based ceramics can be formed into complex shapes, for example bicycle-style chains that can be used to move items inside furnaces at high temperatures. Doped mullite can be used as a laser material.



Kilfinichen Bay, Isle of Mull, near Seabank Villa, with the type locality of mullite in the foreground

The pretty village of Tobermory, home to the mineral tobermorite, roughly  $Ca_3Si_6O_{16}(OH)_2 \cdot nH_2O$ , is 27 km north of Kilfinichen Bay. Tobermorite is not quite such a high-flier as mullite, but WoS still leads you to 485 articles and 800 citations in 2009. Its citation rate is increasing exponentially. The mineral was discovered in 1880, in amygdaloids in basalt, by a man who was, in every sense, a giant of Scottish mineralogy, Matthew Forster Hedde. Professor of Chemistry at the University of St. Andrews, he tramped single-mindedly around Scotland collecting minerals, which he catalogued, analysed and described, producing hundreds of drawings based on optical goniometry. He had tremendous physical strength, carried hammers up to 28 lbs in weight and thought nothing of using dynamite to reveal the 'hidden treasures' inside rocks. Tobermorite is a cement phase, a very complicated material, with a range of imperfectly understood polymorphs and chemical variants. It is a crystalline product of gentle heating of the poorly crystalline calcium silicate hydrates that are the main binding material in Portland cement, so its performance is crucial where cements are used in warm environments, such as petroleum reservoirs and radwaste

<sup>1</sup> There is more literature research underlying these little articles than you might think, and I'm greatly indebted to Ross Angel, of Virginia Tech, for running down an American reference confirming this exact locality.



Tobermory



Tobermorite, Concepcion del Oro Mine, Zacatecas, Mexico. Sample (3.9 × 2.3 × 1.9 cm) MARTIN ZINN. PHOTO COURTESY WWW.IROCKS.COM



Kilchoan. The hills are part of the Ardnamurchan ring complex.

repositories. It forms in the altered rinds on glass radioactive waste-forms and at interfaces between cement grouts and clay, and can be used for its ion-exchange properties, including removal of the radionuclides <sup>137</sup>Cs and <sup>90</sup>Sr from liquids.

From Tobermory a half-hour ferry trip north across the Sound of Mull brings us to the tiny village of Kilchoan, the most westerly village of mainland UK. Kilchoanite,  $Ca_6(SiO_4)(Si_3O_{10})$ , is the Cinderella of our three minerals, with a mere 17 articles and 110 citations since its identification as a mineral in 1961 by S.O. Agrell and P. Gay from Cambridge. Like tobermorite it is a phase related to cement, and like mullite it was discovered first as a synthetic compound, by one of the most enduring contributors to cement science, Della M. Roy of Penn State. In 1958 she synthesised a phase in the system  $CaO-Al_2O_3-SiO_2-H_2O$ , at about 800 °C and 100 MPa, that she called phase Z. Agrell and Gay identified the same phase, using XRD, in limestones metamorphosed by gabbros of the Ardnamurchan ring complex.

Mullite, tobermorite and kilchoanite provide a fascinating glimpse of the interweaving of mineralogy and materials science. And the tea-rooms and pubs of Tobermory are highly recommended!

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