The scandium phosphate pretulite has been identified with scandian zircon and xenotime-(Y) in an apatite-rich oolitic Ordovician ironstone at Saint-Aubin-des-Châteaux, Armorican Massif, France. Pseudo-octahedral crystals of pretulite, up to 400 μm across, have grown epitactically on detrital zircon. They reveal complex zoning due to incorporation of Y and HREE, as well as to an extended solid-solution toward the zircon end-member. Characteristic compositions in the pretulite – xenotime-(Y) – zircon system are: PrL0.973 Xnt0.020 Zrn0.007, PrL0.907 Xnt0.088 Zrn0.005, PrL0.875 Xnt0.062 Zrn0.005, PrL0.718 Xnt0.024 Zrn0.258, and PrL0.453 Xnt0.042 Zrn0.505. A single-crystal X-ray refinement of the structure in space group I41/amd (R = 0.0389) gives a = 6.5870(9), c = 5.809(1) Å, for the formula (Sc0.904Y0.032HREE0.016Zr0.048)(P0.952Si0.048)O4. The Raman spectrum is presented. Detrital zircon shows phosphate-rich metamict zones containing HREE and Sc (up to 3.2 wt.% Sc2O3). Analytical and crystallographic data suggest a complete solid-solution between zircon and pretulite. Xenotime-(Y), also epitactic on zircon, shows distinct stages of crystallization, with a decrease in Y together with an enrichment in the lighter REE and Sc (up to 0.7 wt.% Sc2O3). The scandium minerals at Saint-Aubin reflect the evolution of the iron ore, from sedimentation to diagenez and metamorphism, followed by multistage hydrothermal leaching and recrystallization. Despite the high concentration of Fe in the environment, this unique occurrence of Sc minerals illustrates the high capacity of the phosphate ion to extract scandium and precipitate it as a specific phase, at relatively low-temperature conditions.

Keywords: scandium, phosphate, pretulite, zircon, xenotime-(Y), iron ore, Ordovician, Armorican Massif, France.

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Un phosphate de scandium, la prétulite, a été identifié, en association avec du zircon et du xénotime-(Y) scandifères, dans un minerai de fer oolithique ordovicien riche en apatite à Saint-Aubin-des-Châteaux, Massif Armorican, en France. Les cristaux pseudo-octaédriques de prétulite (jusqu’à 400 \( \mu \text{m} \)) sont en surcroissance épitaxique sur du zircon détritique. Ils montrent une zonation complexe due à l’incorporation du Y et des terres rares lourdes, ainsi qu’à une solution solide étendue vers le pôle zircon. Des compositions-types dans le système prétulite – xénotime-(Y) – zircon sont: Prl0.973Xnt0.020Zrn0.007, Prl0.907Xnt0.088Zrn0.005, Prl0.873Xnt0.042Zrn0.028 et Prl0.453Xnt0.042Zrn0.505. L’affinement de la structure cristalline aux rayons X sur monocristal (groupe spatial \( \text{I} \frac{41}{1} \text{amd} \), \( R = 0,0389 \)) a été fait avec \( a = 6,5870(9) \), \( c = 5,809(1) \text{\AA} \), sur la base de la formule \( (\text{Sc}0,904\text{Y}0,032\text{TRL}0,016\text{Zr}0,048)(\text{P}0,952\text{Si}0,048)\text{O}4 \). Le spectre Raman est présenté. Le zircon détritique montre des zones métamictes riches en phosphate, avec terres rares lourdes (TRL) et scandium (jusqu’à 3,2% pds Sc\(_2\text{O}_3\)). Les données tant analytiques que cristallographiques suggèrent une solution solide complète entre prétulite et zircon. Le xénotime-(Y), également en épitaxie sur le zircon, montre plusieurs stades de cristallisation, traduisant un appauvrissement en Y corrélatif d’un enrichissement en faveur de terres rares plus légères, ainsi qu’en scandium (jusqu’à 0,7% pds Sc\(_2\text{O}_3\)).

La minéralogie du scandium à Saint-Aubin reflète l’évolution du minerai de fer: sédimentation, diagenèse et métamorphisme, et enfin lessivage et recristallisation par des venues hydrothermales polyphasées. Malgré la haute concentration en fer de l’environnement, cette occurrence très particulière illustre la forte capacité de l’ion phosphate à se combiner au scandium et à le précipiter sous forme d’une phase minérale spécifique à relativement basse température.

Mots-clés: scandium, phosphate, prétulite, zircon, xénotime-(Y), minerai de fer, Ordovicien, Massif Armorican, France.

### INTRODUCTION

Scandium is rarely expressed as specific mineral species, owing to its dilution in common silicates, where it substitutes for Fe, Mg and Al. There exist at present only nine approved species of scandium minerals: six silicates (bazzite, thortveitite, cascandite, jervisite, scandiobabingtonite and kristiansenite), and three phosphates (kolbeckite, pretulite and juonniite) (Mellini et al. 1982, Orlandi et al. 1998, Hey et al. 1982, Bernhard et al. 1998b, Liferovich et al. 1997, Raade et al. 2002).

Pretulite was discovered at Höllkogel, in eastern Austria, by Bernhard et al. (1998b), who described numerous occurrences within quartz–lazulite veins in the Lower Austro-alpine Grobneis complex. Another probable occurrence of pretulite was incompletely described as an unnamed Sc phosphate by Novák & Srein (1989) in the Dolní Bory pegmatites of western Moravia, Czech Republic. The present study deals with a new occurrence of pretulite, identified in a sandstone quarry located at Saint-Aubin-des-Châteaux, Loire-Atlantique, in western France. Here, pretulite is closely associated with scandian zircon and xenotime-(Y) within a sedimentary iron ore showing a complex paragenetic evolution. This occurrence presents new insight concerning aspects of the geochemistry and crystal chemistry of scandium.

### GEOLOGICAL SETTING AND PETROLOGY

Figure 1 gives the geographic location of the quarry of Saint-Aubin-des-Châteaux. This quarry is situated in the lower member of the Grès armoricain Formation, of Arenigian age. This member is mainly composed of sandstone; at a regional scale, it includes oolitic ironstones (Chauvel 1974) at four main horizons, A to D, from top to bottom. These ironstones have been mined in the past (Puzenat 1939). According to Chauvel (1974), they are essentially composed of iron oxides (magnetite, hematite, ilmenite), silicates (chlorite, stilpnomelane) and quartz, siderite, pyrite and apatite. The phosphate is ubiquitous (mean concentration over 2 wt.%; up to 6 wt.% in the B horizon).

In the Saint-Aubin quarry, only the A horizon is well developed. It is mainly composed of siderite and chlorite, but locally very enriched in Sr-bearing fluorapatite (4 wt.% SrO: Chauvel & Phan 1965). It was affected by diagенesis and very low grade metamorphism. The primary sedimentary features, where preserved, consist of millimetric layers of oolites. Some of these layers are enriched in fluorapatite (abundant), or minor detrital.
titanium oxides and zircon. Carbonaceous phases (organic matter and late graphite) are disseminated throughout the rock, giving it a characteristic black color. SEM examinations reveal rare minute crystals of galena, sphalerite and monazite-(Ce). Pretulite and xenotime-(Y) are only present as epitactic overgrowths on zircon crystals.

The primary texture was later altered by hydrothermal processes (at least three stages of hydrothermal activity), as indicated notably by the presence of massive pyrite, together with minor base-metal sulfides like marcasite, galena, and sphalerite (Herrouin et al. 1989, Moëlo et al. 2000, Gloaguen 2002). Centimetric to decimetric veinlets of quartz, siderite, pyrite and lulzacite (a recently described Sr–Al–Fe phosphate: Moëlo et al. 2000, Léone et al. 2000) were formed within the ironstone (incorrectly called “limestone” in Moëlo et al. 2000). Hydrothermal processes have also transformed the ironstone itself locally by recrystallization of siderite, dissolution and recrystallization of Sr-rich fluorapatite, crystallization of graphite lamellae at the expense of organic matter, and formation of a red-brown variety of chlorite.

**Pretulite**

**Descriptive aspects**

Pretulite was first discovered in an apatite-rich fragment from the A horizon, showing numerous submillimetric hexagonal platelets of “red-brown chlorite” (a Mg-poor, Al-rich chamsoite). This fragment was dissolved in HCl; the whole residue contains a dozen crystals of pretulite with a flattened pseudo-octahedral habit (Fig. 2). The main form is the bipyramid {011}, with subordinate basal faces {001}; faces of the prismatic form {110} are rare. The size of these crystals varies from 150 to 400 μm across; they are translucent, yellowish white, with an adamantine luster.

In polished section, one of these crystal appears to be an overgrowth on a rounded crystal of zircon (Fig. 3); xenotime-(Y) also is present. Thin sections made of samples of the A horizon show other crystals of pretulite, invariably as an epitactic overgrowth on zircon crystals (Fig. 4); gangue minerals are chamsoite with fluorapatite and graphite.

**Chemical characterization**

Imaging by scanning electron microscopy (SEM) and with back-scattered electrons (BSE) invariably reveals the presence of chemical zoning in the crystals of pretulite. Figure 3 reveals a complex pattern of growth-induced zoning, showing schematically first a dark grey core (A zone), secondly, a narrow intermediate rim (B zone, light grey), then a wide grey outer zone (C zone), and finally (at the opposite side) a thinner white layer located close to the zircon crystal (D zone). These zones were characterized chemically by elemental mapping and quantitative electron-probe micro-analysis (EPMA; Figs. 5a-d, Table 1).

In the A zone (anal. 1–7), the pretulite is the richest in Sc, with low contents of yttrium (1.2 to 3.0 wt.% Y₂O₃) and heavy rare-earth elements (HREE) (mostly

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**FIG. 2.** SEM–BSE image of a euhedral crystal of pretulite (left), and proposed crystal forms (right): combination of main {011} bipyramid with minor {001} and rare {110}.
Fig. 3. Overgrowth of a zoned crystal of pretulite (~150 × 50 μm), together with a crystal of xenotime-(Y) (Xnt) over a detrital zircon crystal. SEM-BSE image of a polished section. Central zone A (dark grey): REE- and (Zr, Si)-poor pretulite; intermediate zone B (light grey) enriched in REE and (Zr, Si); zone C (medium grey, upper and right border): REE-rich pretulite; zone D (white rim close to zircon): (Zr, Si)-rich pretulite.

Fig. 4. Epitactic overgrowth of euhedral pretulite (Ptl, grey-black), with an external Zr-rich rim (Ptl(Zr), light grey) at the two opposite ends of a detrital crystal of zircon (Zrn, light grey). The white zones correspond to an epitactic overgrowth of xenotime-(Y) (Xnt). Chlorite (Chl) with graphite lamellae (within black area) is the matrix mineral. A smaller zircon – xenotime-(Y) – pretulite aggregate is visible at right. SEM–BSE image; for clarity, the contrast between the central part [zircon and xenotime-(Y)] and the rest of the image has been attenuated.

Fig. 5. Chemical zoning of a section of a pretulite crystal (see also Fig. 3), observed with EPMA elemental mapping (a to d: Sc, Zr, Y and Yb, respectively). Colors range from violet to red, and indicate an increasing concentration of the element. In a, red areas correspond to zone A of Figure 3; zone D (black) is not visible. In b, well-defined red areas correspond to Zr-rich parts of zone B (center) and to zone D (bottom, with zircon). Individual maps do not allow us to distinguish zone C.
# TABLE 1. RESULTS OF ELECTRON-PROBE MICRO-ANALYSES OF PRETULITE FROM SAINT-AUBIN-DES-CHÂTEAUX

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A, B, C and D: different zones of the crystal shown in Figures 3 and 5; other data pertain to the (Zr, Si)-rich rim of pretulite crystals from a thin section (Fig. 4). Analytical conditions: Cameca microprobe SX 50 (BRGM-CNRS - University common laboratory, Orléans), voltage 20 kV; intensity 20 nA; standards: synthetic pure phosphates (Y, Er, Lu and Dy L₆), synthetic zircon (Zr/L₆), synthetic hafnium oxide (Hf/L₆), synthetic pretulite (Sc/K₂ and P/K₂), albite (Si/K₂), synthetic corundum (Al/K₂), hematite (Fe/K₂), detection limit of the elements (wt.%): Al, Si 0.015, P 0.02, Ca 0.03, Fe, Sc 0.05, Hf 0.07, Zr 0.09, Y 0.10, REE 0.11, Th 0.20; - below detection limit; n.d.: not determined.
Yb, then Er, Dy and Lu, with a total below 1.3 wt.% of the respective oxides); zirconium and silicon contents are very low, below 0.6 wt.% ZrO₂ and 0.4% SiO₂. The composition richest in Sc (no. 1) corresponds to the formula: [Sc₀.₉₈(Y₀.₀₁7Yb₀.₀₀₂)O₄.₀₀₁]₀.₀₁(Sc₀.₉₂₉V₀.₀₁₀Al₀.₀₀₁)₀.₀₁(Zr₀.₉₁₅H₀.₀₇₉)₀.₀₂(P₀.₈₈₈Si₀.₃₀₄)O₄.₀₀₁, or Prt₀.₉₀₀Xnt₀.₀₁₁Zrn₀.₁₈₉. In the B zone (nos. 8–9), the pretulite shows a significant enrichment in Zr and Si, up to 6.9 wt.% ZrO₂ and 3.4% SiO₂. Composition 9 corresponds to [Sc₀.₈₅₈(Y₀.₀₂₂Yb₀.₀₀₁Er₀.₀₀₁Lu₀.₀₀₁)O₄.₀₄₁]₀.₀₁(Zr₀.₈₀₃)O₄.₀₁₈, or Prt₀.₈₇₇Xnt₀.₀₁₄Zrn₀.₀₉₅.

In the C zone (nos. 10–14), the pretulite shows minor amounts of Zr and Si (below 2.8% ZrO₂ and 1.4% SiO₂), with an enrichment in Y (up to 4.3% Y₂O₃) and HREE (especially Yb, up to 2.5% Yb₂O₃). The composition richest in (Y, HREE), no. 10, corresponds to [Sc₀.₉₀₈(Y₀.₀₅₇Yb₀.₀₁₉Er₀.₀₀₆Lu₀.₀₀₄)O₄.₀₉₆]₀.₀₁₃, or Prt₀.₈₉₇Xnt₀.₀₁₃Zrn₀.₀₇₈. In the D zone (nos. 15–19), the pretulite reveals high Zr and Si contents (17–20% ZrO₂ and 9–11% SiO₂); minor quantities of Y and Yb are present in similar proportions (about 1 wt.% of the respective oxides). Composition 19 corresponds to [Sc₀.₇₀₂(Y₀.₀₁₇Yb₀.₀₀₁)O₄.₀₁₈]₀.₀₁(Zr₀.₂₅₈H₀.₀₆₄)₀.₀₂(Zr₀.₈₅₈Si₀.₂₈₀)O₄.₀₀₃, or Prt₀.₇₁₇Xnt₀.₀₂₆Zrn₀.₅₈₈.

In all cases enriched in Zr and Si (over 0.02 atoms per formula unit, apfu), the atomic ratio Zr/Si is invariably close to 1, in agreement with a solid-solution scheme according to the coupled heterovalent substitution Sc³⁺ + P⁵⁺ ↔ Zr⁴⁺ + Si⁴⁺; the molar ratio ScPO₄/ZrSiO₄ attains 2.8.

Diffraction data were used to solve the average structure of this sample of pretulite. Table 4 gives the coordinates of the atoms in the unit cell. Owing to its complex chemical composition, the structure was refined by 1) adjusting the Sc/Zr value, and, accordingly, the P/Si value, and 2) adjusting the Sc/Y, HREE value, considering all heavy rare-earth elements (HREE) as Yb, with Sc/Y and Yb/Y values close to the mean of Sc/Y and HREE values indicated by the electron-microprobe data (Table 1). The best R value (0.039) was thus obtained for the simplified structural formula [Scₓ₀.₉₀₄Yₓ₀.₀₃₂(YbₓHREE)₀.₀₁₀Zrx₀.₀₄₈]₀.₀₂₅(Oₓ₀.₉₂₇Si₀.₈₄₈)O₄, close to a composition of the C zone. This solution represents an average structure of a relatively inhomogeneous crystal, which explains the lower accuracy of these data compared to those of Bernhard et al. (1998b) (R = 0.019) for the Austrian pretulite. Nevertheless, the relatively low R value, as well as the homogeneity of Y factors, indicate that this solution is a good approximation of the real structure. A listing of observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

According to Table 3, the a and c parameters increase in going from pure synthetic ScPO₄ to the pretulite from Saint-Aubin owing to the substitution of larger cations, Y and HREE, for Sc, as well as to the presence of the zircon component. The two natural examples of pretulite have very close unit-cell volumes, but a higher density (3.83 g/cm³) was calculated for the Saint-Aubin material owing to its enrichment in the heavier elements.

TABLE 2. DATA ON THE CRYSTAL OF PRETULITE FROM SAINT-AUBIN-OHES-CHATEX LS/CMOS/ outweigh the structure refinement, and experimental details

<table>
<thead>
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<th>Crystal data</th>
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<tr>
<td>Simulated structural formula</td>
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<td>a</td>
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<tr>
<td>c</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Absorption coefficient</td>
</tr>
</tbody>
</table>

Data Collection

| Temperature | ambient |
| Radiation | MoKα (λ = 0.71073 Å) |
| Diffraction | 2θ range 20–28°; step size 0.05°; g range 0–25° |
| Crystal-to-detector distance (ID) | 50 mm |
| Reflectivity | 10598 |
| Reflections collected | 5048 |
| R(refl) | 0.0602 |

Refinement

Refinement method: Full-matrix least-squares on F²
Date/retransmission/parameter | 1998/10/15 |
| Goodness-of-fit on F² | 2.466 |
| R index (all data) | 0.0508 |
| Largest diff. peak/hole | 0.518, -0.729 e Å⁻³ |

Crystallography

Despite its relatively large size, the pretulite crystal shown in Figure 2 was used for a single-crystal X-ray study, with an imaging plate system. Operating conditions and related data are given in Table 2. On the basis of its tetragonal symmetry, the unit-cell parameters of the Saint-Aubin material are a = 6.5870(9), c = 5.809(1) Å. Table 3 and Figure 6 compare these new data with those of pretulite from the type locality, pure synthetic ScPO₄, and related isotopic compounds (synthetic YPO₄, zircon and various HREE phosphates).
Raman spectroscopy

The Raman spectrum of pretulite is presented for the first time; it was obtained on the largest crystal shown in Figure 4, as well as on a sample (HK1A) from the type locality, provided by F. Bernhard. As the presence of REE in pretulite induces strong fluorescence lines, pure synthetic ScPO₄ (provided by Eugene Jarosewich), used as Sc standard for the electron-probe micro-analyses, also was studied for comparison. Data were obtained with a DILOR XY800 Raman microprobe (BRGM – CNRS – Université d’Orléans, Dr. J.-M. Bény, ISTO-CNRS, Orléans, analyst). Operating conditions were: Ar⁺ laser, λ of the exciting radiations 488 and 514.5 nm, 25 mW (~3 mW on the sample), recording window 60–2020 cm⁻¹, objective ×100, and acquisition time 120 s.

The spectra obtained on pretulite from Saint-Aubin with the two laser sources allow us to distinguish complex groups of strong REE-fluorescence-induced bands from fine specific Raman bands (Fig. 7a). A comparison of the Raman spectrum of pretulite from the type locality with that of REE-free synthetic ScPO₄ (Fig. 7b) confirms the discrimination between fluorescence and Raman bands. All three samples present eleven well-defined Raman bands (Raman shift in cm⁻¹): a very strong pair at 1079–1082 and 1024–1026, with an intermediate doublet at 1049–1053 and 1043–1045, then seven medium to weak bands at 595, 474–475, 331–334, 326, 240–243, 234 and 186–187. This Raman spectrum is similar to that obtained for xenotime-(Y) (C. Bény, unpubl. data), but with an increase of about 30 cm⁻¹ of the Raman shift of the two strongest bands.

SCANDIAN ZIRCON

Zoned detrital zircon

The finely stratified ironstone shows numerous detrital crystals of zircon, generally with titanium oxides in peculiar millimetric layers. In reflected light and SEM-BSE images, these zircon crystals commonly display concentric zoning (Fig. 8) indicative of a primary oscillatory growth. The usually anhedral to subhedral morphology of the zircon crystals, which cuts this growth zoning, clearly indicates their detrital origin, without recrystallization. This kind of zircon was described in iron ores of Lower Ordovician age by Chauvel (1968, 1974), as well as in rutile- and zircon-rich sandstones from the Armorican Massif by Faure (1978).

![Image](1663.png)
Nevertheless, in the A horizon at Saint-Aubin, the proportion of such zoned crystals (about one third) is particularly high.

Results of the electron-probe micro-analyses are given in Table 5. The dark zones correspond to a phosphate enrichment, together with Sc, Y, Yb, Er, Fe, Ca and Al (and, in some cases, Lu and Tb; U is below detection limit). These dark zones give low analytical totals, from 95 down to 92 wt.%, whereas the light zones (pure zircon) give totals close to 100 wt.%. Such a deficit is not strictly correlated with the cumulative sum of P and associated cations, and could not be explained by the omission of less abundant HREE, or LREE in the analytical process. It reveals a metamict state of these zones, enriched in H2O (maximum ~5–8 wt.%). It is well known that there is a positive correlation among Y, U and P in zircon (see, for instance, Köppel & Sommerauer 1974), which explains the indirect correlation observed between Y (and the REE) and the metamictization process (Larsen et al. 1953).

An increasing P content is correlated positively with the amount of HREE, Y and Sc (but negatively with Fe, at high P contents). The level of scandium reaches 3.18 wt.% Sc2O3 for the composition richest in P (8.2 wt.% P2O5), which corresponds to the formula (without H2O):

$$Zr_{0.76}Hf_{0.01}[Sc_{0.09}Y_{0.07}(HREE)_{0.03}]P_{0.19}Al_{0.03}Fe_{0.03}$$

CaO0.02(SiO2.75P0.22)O4.02. In the light zones, P, Sc, Ca and Al are below detection limits, and HREE and Fe decrease significantly; only hafnium is systematically present (0.8 to 2.3 wt.% HfO2), as in all crystals.

According to Geisler & Schleicher (2000) and Geisler et al. (2001), a significant Ca content (>0.2 wt.% CaO) in the metamict zones of zircon is indicative of hydrothermal leaching or of weathering, which introduces Ca (and probably Fe, Al and Mn), with a loss of Zr, Si and radiogenic Pb (possibly U also). In contrast, at Saint-Aubin, Y, Sc and the HREE are clearly primary, to counterbalance the phosphate anion, and the zoning of zircon indicates an oscillatory growth between end-member zircon and a phosphate-type component [a mixture of pretulite and xenotime-(Y)].

Except for scandium, all minor elements detected in the zoned crystals are commonly found in natural zircon (Deer et al. 1997). An analysis for scandium is generally omitted in analytical work on zircon. However, this element may commonly be present as a minor component together with Y and HREE in phosphorus-rich varieties of this mineral. Among others, Romans et al. (1975) have demonstrated that scandium is systematically present, with a mean content of 0.2 wt.%, in the magnetic fraction of zircon enriched in Y and P from three commercial concentrates, with a maximum of 0.7 wt.% Sc in a zoned crystal (together with 7.5% Y and 4.1% P). Zircon with about 1 wt.% Sc2O3 has been discovered at Baveno (Italy) by Gramaccioli et al. (2000). Another example is an exotic occurrence of a “solid solution of zircon and xenotime-(Y)” described recently by Mordberg et al. (2001) in the Schugorsk bauxite deposit, in Russia. This phase crystallized during bauxite weathering at the contact between zircon and xenotime grains. Chemically, it corresponds to zircon with up to 5.8 wt.% Y2O3, and 3.3% Sc2O3 (and up to 3.8% P2O5), but the level of the HREE was apparently not established (total below 92 wt.%). This composition is very close to that of the zones richest in P in the detrital zircon from Saint-Aubin.
Fig. 7. Raman spectra of natural and synthetic pretulite. (a) (top): two spectra of pretulite from Saint-Aubin-des-Châteaux with two laser sources ($\lambda = 488$ and 514.5 nm); non-indexed lines are REE fluorescence bands. (b) (bottom): spectra at $\lambda = 514.5$ nm for pretulite from the type locality (Höllkogel, Austria), and for synthetic ScPO$_4$ (fluorescence bands absent). Intensity scale bar in arbitrary units.
### TABLE 5. COMPOSITION OF DETRITAL ZIRCON COEXISTING WITH PRETULITE FROM SAINT-AUBIN-DES-CHÂTEAUX, FRANCE

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</table>

Phosphorus-rich compositions (columns 1 to 4) correspond to dark growth-zones, as in Figures 8 and 10. Columns 7, 8, 10 and 11 correspond to the zircon crystal shown in Figure 9. Analytical conditions: see Table 1. Additional standards: synthetic Gd phosphate (GdPO₄), Durango apatite (Ca FAP), synthetic thorianite (ThPO₄). - : below detection limit. H₂O*: maximum content in metamict zones, assuming a total of 100 wt %. Compositions are expressed in weight % on the left, and in terms of cation proportions on the right (cation total = 2 atoms).
Neoformation of a zircon-type compound with an unusual composition

A systematic SEM–BSE examination of one thin section revealed the sporadic development of a micro-crystalline rim around some crystals of zircon. Such a rim may appear on one side of the crystal, with an oscillatory development (Fig. 9a), or all around the detrital core (Fig. 9b). In some cases, the overgrowth seems to replace an initial volume of zircon, i.e., as a result of a solution-and-redeposition process. According to Ewing (2001), such a local destabilization of zircon could be due to a leaching process under hydrothermal conditions.

A SEM–EDS analysis reveals a complex chemical composition, but the rim seems homogeneous in each case. In Figure 9a, the rim contains major amounts of Zr, Sc, Si and P, with minor Fe (4 wt.% Fe₂O₃), Y (2.5% Y₂O₃), Hf, Ca, Sr, Yb and U (approximately 1–1.5% of the respective oxides). The formula is: (Zr₀.₄₉Hf₀.₀₁)₂₀.₅₀[Sc₀.₄₂Y₀.₃₆(HREE)₀.₀₁]₁₂₀.₄₇U₀.₀₆Sr₀.₀₂Fe₀.₁₀Ca₀.₀₅(Si₀.₅₁P₀.₃₆)₁₈₀.₈₇O₄.

The rim shown in Figure 9b contains major amounts of Zr and Si (35% ZrO₂ and 17% SiO₂, mean result of three spot analyses), along with (wt.% of the respective oxides): Fe 5.7, P 8.0, Y 4.3, Sc 4.3, Ca 2.2, U 1.8, Sr 1.6 and Hf 1.5. Not considering Fe, Ca, Sr and U, this composition is close to 70% ZrSiO₄, 20% ScPO₄ and 10% YPO₄. Like for the composition of the dark zones within detrital zircon, the totals are low (80 to 90 wt.%), probably owing to partial or complete metamictization (leading to a high H₂O content), but also reflecting the fine-grained texture of the rim.

SCANDIAN XENOTIME-(Y)

Detrital crystals of zircon very commonly show an epitactic overgrowth of anhedral to subhedral xenotime-(Y) crystals (Figs. 4, 8), as has been observed in other deposits (i.e., Petersen & Secher 1993). Such an over-
growth is generally related to hydrothermal processes, but a diagenetic formation also is possible (Fletcher et al. 2000, Cabella et al. 2001). Figure 10 presents another well-developed example, where a zoned crystal of zircon is nearly completely surrounded by xenotime-(Y). The inner zone of xenotime-(Y) (Xnt2a), at the contact with zircon, presents a porous texture (“poikilitic crystallization”), whereas an outer zone (Xnt2b) has virtually no pores. A third zone (Xnt2c) is visible as a very fine light rim (less than 2 μm thick). Such a zoning has been observed in various crystals, and indicates multistage crystallization. Minute inclusions of galena have been observed in some cases in such overgrowths of xenotime-(Y).

Results of electron-probe micro-analyses of xenotime-(Y) are given in Table 6. Among the REE,holmium has been omitted, and some minor interferences involving REE emission lines (Roeder 1985) have been neglected. Nevertheless, it appears that the zoning of xenotime-(Y) is directly related to a decrease in the amount of Y, from the contact with zircon to the rim, together with a zonation in the distribution of the REE.

In the first generation of xenotime-(Y), Xnt1 and Xnt3a have quite similar compositions, very close to that of Xnt2a (Xnt1, 2 and 3: distinct crystals). The major REE are Yb (7.0 to 7.3% Yb₂O₃), Er and Dy (up to 5.5 wt.% of the respective oxides), with minor Gd (less than 1.1% Gd₂O₃). The scandium content is around 0.2% Sc₂O₃. Iron, not detected in Xnt1, is over 1% Fe₂O₃ in Xnt2a.

In the second generation of xenotime-(Y), Xnt2b and Xnt3b show a marked increase of middle REE (Dy from 7.4 to 8.7% Dy₂O₃, Gd from 3.2 to 4.2% Gd₂O₃), with a corresponding depletion in Er and Yb (below 4.5% of the respective oxides). The Lu content is the same, Fe slightly increases, whereas Sc reaches 0.7% Sc₂O₃; this Sc maximum for Xnt2b corresponds to the formula [Y₀.₆₇₈(Dy₀.₀₈₀Er₀.₀₄₆Yb₀.₀₄₅Gd₀.₀₃₅Tb₀.₀₁₁Lu₀.₀₀₆)₀.₂₂₃Sc₀.₀₂₂Fe₀.₀₄₇Ca₀.₀₀₂]₀.₉₇₂P₁.₀₂₉O₄.₀₅₅.

In the third generation of xenotime-(Y), the composition (Xnt2c) is close to that of Xnt2b, but with the addition of significant Sm and Eu contents (1.6% Sm₂O₃ and 0.8% Eu₂O₃). Uranium has been also detected (0.8% UO₂).

Scandium is invariably present, in the range 0.2–0.7 wt.% Sc₂O₃. Bernhard et al. (1998a) indicated a higher Sc content in uranium-rich xenotime-(Y) (1.9–2.7 wt. % Sc₂O₃) from Höllkogel, the type locality of pretulite. Such a strong chemical contrast between generations of xenotime-(Y) at the crystal scale has rarely been documented. Sabourdy et al. (1997) indicated a similar enrichment in the middle REE Gd and Dy, and a corresponding decrease in Yb, from the center to the rim in alluvial crystals of xenotime-(Y) from the Limousin (Massif Central, France). They considered this zoning to be primary (magmatic). Bernhard et al. (1998a) presented SEM–BSE images of strongly zoned crystals of xenotime-(Y) from eastern Austria. At Saint-Aubin, there is a strong chemical discontinuity between zones of xenotime-(Y), as indicated also by the variation between zones a and b of the ratio of the middle to the heavy REE [(Gd + Dy) / (Er + Yb), Table 6] from 0.27 to 1.28 in Xnt2, and from 0.51 to 1.98 in Xnt3. Such a contrast necessarily reflects quite distinct thermochemical conditions of crystallization, acting at different paragenetic stages.

**SOLID SOLUTIONS WITHIN THE TERNARY SYSTEM ScPO₄ – (Y,HREE)PO₄ – ZrSiO₄**

All our analytical data (SEM–EDS and EPMA) on pretulite, zircon and xenotime-(Y) have been plotted in terms of ScPO₄ – (Y,HREE)PO₄ – ZrSiO₄ (Fig. 11), together with data from the literature. Various compositions along (or close to) the zircon–pretulite join have been encountered, and further data would very probably fill the whole chemical spectrum between the two end-members. This plot thus suggests a continuous solid-solution between zircon and pretulite, corresponding to the heterovalent substitution Zr⁴⁺ + Si⁴⁺ ↔ Sc⁴⁺ + P⁵⁺.
Fig. 10. Zoned crystal of zircon with an epitactic overgrowth of xenotime-(Y) (SEM–BSE image). Darkest growth-zones of zircon correspond to (Y,REE,Sc)- and P-enriched compositions. Xenotime-(Y) shows three distinct zones: inner zone Xnt2a (porous, light grey), outer zone Xnt2b (white grey), and fine rim Xnt2c (white).

### Table 6. Electron-Microprobe Data on Xenotime-(Y) from Saint-Aubin-Désert-Château, France

<table>
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<tr>
<th>Anal.</th>
<th>Xnt2a</th>
<th>Xnt2b</th>
<th>Xnt2c</th>
<th>Xnt2a</th>
<th>Xnt2b</th>
<th>Xnt2c</th>
<th>Xnt2a</th>
<th>Xnt2b</th>
<th>Xnt2c</th>
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<td>wt. % oxide</td>
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Xnt1: sample shown in Figure 1; Xnt2a: sample shown in Figure 10 (at inner porous zone); Xnt2b: sample shown in Figure 10 (at outer porous zone); Xnt2c: sample shown in Figure 10 (at white external rim); Xnt3: sample shown in Figure 10 (at white external rim). At data (atomic ratio) from Tables I and 5, elements programmed, not detected.

Xnt: sample shown in Figure 1; Xnt2a: sample shown in Figure 10 (at inner porous zone); Xnt2b: sample shown in Figure 10 (at outer porous zone). At data (atomic ratio) from Tables I and 5, elements programmed, below detection limit.
(although one cannot totally exclude a syntactic intergrowth at a submicrometric scale). On the contrary, there is a large miscibility-gap between pretulite and xenotime-(Y), as shown initially by Bernhard et al. (1998a, b). Compositions of detrital zoned crystals of zircon give a linear trend, with an atomic ratio Sc/\((Y,\text{REE})\) close to 1. Data on the zircon – xenotime-(Y) join are scarce; Deer et al. (1997) cited two cases of zircon from Japan with a \((Y,\text{REE})\) content close to 10 wt.% of the oxides, which corresponds to about 20 mol.% substitution. Romans et al. (1975) gave another example with about 25 mol.% substitution. These data are in accordance with the experimental study of Finch et al. (2001), which proved a wide miscibility-gap between zircon and xenotime-(Y).

The unit-cell volume of pretulite is closer to that of zircon than that of xenotime-(Y) (Table 3, Fig. 6): \(V_{\text{Ptl}} = 250.6,\ V_{\text{Zrc}} = 261.0,\ V_{\text{Xnt}} = 286.5\ \text{Å}^3;\ \delta V_{\text{Zrc}/\text{Zrc}} = –4.0\%;\ \delta V_{\text{Xnt}/\text{Zrc}} = +9.8\%\). These findings imply that the substitution \(\text{Sc}^{3+} + \text{P}^{5+} \leftrightarrow \text{Zr}^{4+} + \text{Si}^{4+}\) should be easier than the substitution \((Y,\text{REE})^{3+} + \text{P}^{5+} \leftrightarrow \text{Zr}^{4+} + \text{Si}^{4+}\), which would favor an extensive solid-solution between zircon and pretulite.

In zircon, the simultaneous incorporation of Sc and \((Y,\text{REE})\) will minimize the volume change, and thus enlarge the field of solid solution near the zircon end-member. This inference may explain the linear chemical trend observed in detrital zoned crystals of zircon.

Another geometric constraint is the variation of the ratio \(c/a\), which decreases from zircon to pretulite \([\delta c/a = –2.8\%]\), then to xenotime-(Y) \([\delta c/a = –3.5\%]\). Such a distortion factor may also favor the solid solution between pretulite and zircon. In any case, in a phosphorus-rich environment, the structure of zircon can better retain scandium in solid solution than yttrium or \(\text{REE}\).

The scarcity of intermediate members in the continuous solid-solution series between zircon and pretulite, as well as in natural \((Y,\text{REE})\)-rich zircon, thus probably is not due to crystal-chemical reasons, but rather to geochemical constraints, \(i.e.,\) probably the rarity of...
coprecipitation of zircon with phosphates of (Y, HREE) or Sc, especially during magmatic processes.

The data of Table 3 also permit a better understanding of the epitaxy of pretulite and xenotime-(Y) on zircon. The a parameter of pretulite is very close to that of zircon, which will favor an epitaxy on the (001) plane, and its growth along [001]; it explains the nucleation of two crystals of pretulite at the opposite sides of the elongation (along the A4 axis) of the main crystal of zircon in Figure 4. This inference was also confirmed by a morphological examination with an SEM of another pretulite–zircon association. On the contrary, the c parameter of xenotime-(Y) is very close to that of zircon, which will favor an epitaxy on a crystallographic plane containing the [001] direction, i.e., a (hk0) plane; the growth of xenotime-(Y) crystal will be favored perpendicular to the A4 axis, as is the case in Figure 4.

**Genetic Model for Scandium-Bearing Minerals at Saint-Aubin**

We propose the following genetic scheme for the formation of Sc-bearing minerals at Saint-Aubin.

The first scandium-bearing mineral is zoned detrital zircon. Pretulite appeared later, but scandium required to grow pretulite crystals [like Y for xenotime-(Y)] cannot be inherited from this primitive zircon. For instance, the large crystal of pretulite in Figure 3 crystallized over a crystal of Sc-free zircon. A diffuse pre-concentration of scandium in the ironstone of the A horizon is necessary; it could lodged in sedimentary phosphates, or in (Fe, Mg)-silicates.

In a second step, the diagenetic and very low-grade metamorphic evolution of the ironstone induced a recrystallization process. Precursor phosphates gave the first generation of Sr-rich fluorapatite, and the bulk of the REE, Y and Sc was released (from phosphates or silicates), giving the first generation of xenotime-(Y) as well as pretulite (A-zone type, with nearly end-member composition). The same process may be proposed for the crystallization of disseminated monazite-(Ce). On the basis of the composition of the chlorite, the temperature did not reach 400°C during this phase (Prof. J.-J. Chauvel, Université de Rennes, pers. commun.).

Hydrothermal processes induced by tectonic events led to the destabilization of this metamorphic association by percolation through the A horizon. The early crystallization of a second generation of fluorapatite, followed by the formation of hulzactite, a Sr–Al–Fe phosphate, in quartz–siderite veins, suggests the partial dissolution of primary fluorapatite, which caused a fraction of its lanthanides to be released. This step could explain the next generations of xenotime-(Y), enriched in lighter REE (Gd and Dy), and of pretulite (B- and C-type zones), enriched in Y and HREE. This scheme would also explain the Sc enrichment of the second generation of xenotime-(Y), the enrichment in Zr and Si of the last generation of pretulite (D-type zone), and the formation of mixed phases with various intermediate compositions between pretulite and zircon.

**Conclusions**

Saint-Aubin is the third geological area in which pretulite is found, after the Austrian type-locality (Bernhard et al. 1999b), and the Dolni Bory pegmatites, in the Czech Republic (Novák & Srein 1989). It is also the third occurrence of scandium minerals in France, after the recent discovery of bazzite in the La Lauzière Massif, Savoie, French Alps by N. Meisser (De Ascencio Guedes & Valverde 2000), and thortveitite in the talc deposit of Trimouns, Ariège, Pyrénées (P. de Parseval, pers. commun.).

Sc-bearing minerals at Saint-Aubin reveal a complex geological and geochemical evolution, which is only partly understood. Whereas most occurrences of scandium minerals are linked to late hydrothermal processes generally related to felsic magmatism, the formation of pretulite at Saint-Aubin is quite unique, without any equivalent up to now. Whereas scandium is generally dispersed in rocks, owing to its crystal-chemical similarity with Fe, Mg and Al, paradoxically, at Saint-Aubin, Sc-bearing minerals are found within an iron ore. Despite the high Fe content of the A horizon, scandium can thus be concentrated in specific Fe-free minerals at low-temperature conditions (supergene to hydrothermal), owing to its strong affinity with phosphate ions (Gramaccioli et al. 2000, Lifervich et al. 1998). Another interesting fact is the late formation of various intermediate compositions between zircon and pretulite, which suggests a complete solid-solution between these two end-members. Implicit in our reconstruction is a local mobility of zirconium in solution at a low temperature.

At Saint-Aubin, the ironstone is particularly enriched in fluorapatite. According to mineralogical and petrographic studies, as well as bulk-rock analyses (Chauvel & Phan 1965, Chauvel 1974), this phosphate appears ubiquitously in all iron ore deposits of the Martigné–Ferchaud Paleozoic syncline. In such phosphate-rich environments, one may thus expect the discovery of new occurrences of diagenetic and metamorphic xenotime-(Y) and pretulite. In fact, Chauvel (1968) described an overgrowth around detrital crystals of zircon in some samples: it may correspond to epitactic xenotime-(Y) (or pretulite ?), rather than to a new generation of zircon. More generally, the presence of these accessory minerals in phosphate-rich metasedimentary rocks, as exemplified by the recent description by Cabella et al. (2001) of authigenic xenotime-(Y) and monazite in pelitic metacherts from central Liguria, in Italy, hold much promise as an indicator of the geological evolution of sedimentary units.

Another interesting problem is the origin of the detrital scandian zircon at a regional scale. According to Chauvel (1974), the ironstone horizons within the lower
member of the Arenigian Grès armoricain Formation are related to the weathering and destruction of Cadomian uplands, which are mainly formed of granitic to granodioritic batholiths. These magmatic rocks could thus be the main source of scandian zircon.

The phosphate-rich sedimentary iron ore at Saint-Aubin-des-Châteaux constitutes a new type of occurrence of scandium-bearing minerals at low-temperature conditions. It opens a new field of investigations of the mineralogy, geochemistry and metallogeny of scandium.

Acknowledgements

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References


SCANDIUM MINERALS IN OOLITIC IRONSTONE, SAINT-AUBIN, FRANCE


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